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ISOBARS IN THE TROPICS—SOME BASIC IDEAS OF TROPICAL METEOROLOGY

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Received March 3, 1947

The weather forecaster depends entirely on the observations that he is able to obtain at the time of forecasting. The meteorological observations that were ordinarily available to a forecaster in India before 1939 were confined to the Indian area comprising of India, Burma, Ceylon and the sporadic observations from the ships in the north Indian Ocean. Some of the forecasting centres got a few observations from Indo-China, Siam, Malaya Iran, Iraq, Aden and Egypt. The attention of the forecaster was therefore focussed to the use of data from regions in and immediately surrounding India and the more distant observations were used only to supplement the usual charts. When the war broke out in East Asia, the observations from the more eastern regions and Burma were cut off. The radio silence had been imposed on ships. It was therefore necessary to improve the network of observatories and communications from the regions belonging to the allies. Observations from Russian Turkestan were received at Poona from May 1942. Those from the islands in the Indian Ocean, East Africa, Arabia, Iraq and Egypt and sometimes Turkey and portions of China began to be received in time for daily forecasting by 1943. The receipt of so many unfamiliar observations necessitated their proper appreciation and improved technique.*

There are available monthly charts for the Indian Ocean area prepared by the various Hydrographic and Naval Services, daily charts for the northern hemisphere for the Polar Year (1932–33) and the daily charts prepared by the India Meteorological Department between 1893 and 1904 with the help of observations, received by post, from distant observatories and ships. While all these charts are instructive and useful to verify any new results that may be deduced with the present data, the daily weather forecaster who gets the data in time for forecasting is likely to observe more closely, check immediately and modify rapidly the technique that can be of greatest use even when some of the data are missing due to failure of communications.

* Substance of a colloquium on the subject in Poona Meteorological Office in Jan. 1943.

Unfortunately the failure of communication in one region or another is a common experience. A more intimate knowledge of Indian conditions applied daily to these data can furnish useful information, which an after-study may not always show up. The daily weather forecasting is interesting like the news, when it is actually fresh, and as each day brings its own weather problems, the past weather fails often to attract the same detailed interest in a worker. While it is difficult to self-analyse one's own deductions, an attempt has been made here and elsewhere to place on record the experience gained and the new results obtained.

Choice of Charts of Observations

The problem that is posed to the weather forecaster increases daily. Agriculture, aviation and operations all need that forecasts over large areas be given for as much time ahead as possible. The type and number of observations have also increased. The weather forecaster's observations include: the surface observations (like barometric pressure, temperature, humidity, present weather, wind speed and its direction at lower levels, visibility, clouds and their movement, past weather and precipitation) taken at definite hours of the day, the pilot balloon observations giving the speed and direction of wind at higher levels, Radio-sondé or aeroplane recordings giving temperature and humidity at higher levels, the atmospherics, the radar observations and special observations from ships and aeroplanes. If all observations are plotted over any big area, the task of absorbing the data and suitably interpreting them in the small amount of time that is available to a forecaster before he puts out his forecast is beyond a human being. By sheer necessity, a forecaster concentrates his attention to a set of observations with which he feels the greatest confidence. To prevent strain, he might choose a chart which has less number of observations for a given area and attempt to forecast mainly with its help, supplemented occasionally by reference to other available charts. The chart containing surface observations, and the charts from the derived quantities (like pressure change, pressure departure, etc.) and the upper wind charts for an area like India and the immediate neighbourhood are sufficient to occupy one completely. The isentropic, constant level, constant pressure charts are all attempts to decrease the total intake of the mind at the time of forecasting. But it must be made clear at the outset, that the surface and its derived charts, the upper wind charts, observations of cloud cells, radar observations and the thermodynamic charts are all cross-sections of the weather-pattern and *cannot* be mutually exclusive. The degree of specialisation that one has had determines one's choice as far as general weather forecasting is concerned;

and when specific requirements are to be complied with, the corresponding charts are referred to.

The surface and its derived charts have an initial advantage that the observations have been taken at definite points of space at related times (comparable) and that the observations are available for a fairly long period so that a reference to past surface data is always possible in case of a new idea or theory. The speed and direction of upper wind have also been available for a few decades at many places though the distribution has become satisfactory only comparatively recently.

When surface charts are drawn, the problem that interests one most in the tropical regions is the relation of the isobars to the winds. It is therefore necessary to look into the question closely.

Relation of Isobars to Winds in the Tropics.*

The dynamical equation of wind is given by the following vectorial equation:

$$d\mathbf{V}/dt = 2\,\boldsymbol{\Omega}\,\mathbf{X}\,\mathbf{V} = -\nabla p - \mathbf{F} - (0, 0\ g)$$

Where

$\mathbf{V}$ is the wind velocity, g is the value of gravity,

$\boldsymbol{\Omega}$ earth's angular velocity,

$\mathbf{F}$ frictional force and

p barometric pressure.

Of the terms, the rotational term (second term) involves the component of earth's rotation in a direction at right angles to the direction of the wind and so involves the latitude of the place ϕ ($2 \mid \Omega \mid \sin \phi$). The term $\sin \phi$ decreases when the latitude of the place approaches the equator. It is usual to treat that, as the equator is approached, the rotational term is negligible and to discuss the equation of the wind without it near the equator. This involves the assumption that the other terms retain the same order of magnitude in the tropics as in the temperate latitudes. Actually this is not always true. In the Indian Ocean area round South India, the assumption is definitely not correct. The pressure gradients found in higher latitudes (say 35° or 40° N.) are of the order of 2 mbs. per 70 miles (or across a degree of latitude) and gradients of 4 to 5 mbs. per 70 miles are not uncommon. But in the lower latitudes (both north and south of the equator) south of India the gradient hardly exceeds 0·4 mbs. per 70 miles (across a degree of

* Part of Colloquia at the Poona Met. Office in June-July, 1945.

latitude) and is generally much less near the equator in the neighbourhood of the Comorin. The gradients are so weak that some workers cease to attach any importance to the pressure values of these places. It is therefore not correct to assume that only the rotational term should be ignored near the tropics and that the pressure gradients term retained when both the terms are decreasing in about the same proportion.

If the rotational term be neglected, it is of course valid to say that the wind direction is guided by the pressure gradient term (which is at right angles to the isobars) when the winds are steady. But if the pressure gradient and the rotational terms are both retained as being equally small the vectorial nature of the equation shows that when the winds are steady, the isobars follow the winds even in the tropics as in the temperate latitudes. Due to friction term whose value is undetermined, even in the steady state, a small deviation may be possible. But the general conclusions that are drawn in the temperate latitudes apply to a great extent near the tropics where the pressure gradients are small.

In the Indian Ocean, during the S. W. monsoon, strong pressure gradients associated with steady winds are encountered on the East African coast (from 2° to 10° N.) and to a lesser extent on the east coast of India. In most other places, either the winds are not steady or the pressure gradients are not steep. In the region of steady winds, it is advantageous to draw isobars to follow the winds and deduce the maximum possible information from the isobaric pattern.

As the pressure gradients are small near the equator or the tropics, the pressure values have to be given correct to a tenth of a millibar at individual stations if they are to be of any use at all. Over the tropical region of N.E. Africa where pressure gradients are steep, some forecasters might be satisfied with pressure readings correct to a millibar.

Isobaric Patterns

This is really an application of methods used in many branches of Science. In Hydro-dynamics, given the velocity at discrete points, sources and sinks are constructed easily. In similar branches like Electricity and Magnetism isopleths are drawn to determine most of the fundamental ideas. Naturally many workers assume the methods to be almost axiomatic.

The drawing of isobars requires experience and judgement. When relatively flat pressure areas or regions of few observations are encountered, considerable latitude exists in the method of drawing isobaric patterns. It is often mentioned by older officers that in the Indian area, Hemraj used the

geometry of isobars very effectively. Unfortunately, little has been left on record of his method. It has been found that a careful drawing of isobars can indicate movements of disturbances which are not obvious from mere observations and a cursory study. They also indicate approximately the regions of partitions of air masses.

In higher latitudes, the earth's rotational term would be predominant. If further, one considers a few kilometres above ground in those latitudes even the frictional force can be considered negligible. In those latitudes and at those higher levels, the isobars and the streamlines are practically the same. That is the ideal condition. In practice, an approximation to the ideal condition would be suggestive. Even at the surface in other latitudes, the isobaric pattern, that tends to approximate to the streamlines, gives more information. In drawing the isobars, when one takes account of both pressure and wind direction, this approximation is inevitably carried out.

With the risk of repeating rules which might have been used by many, a few of them are given here. All isopleths have to be similarly considered though isobars being the most important are dealt with here.

The isobars should appear to belong to a family of curves, so that the closed (low or high) pressure areas become the nodal curves; and the wedges, ridges, or troughs become the natural cusps of the family.

If there be two closed (low or high) pressure areas, the next isobar drawn to enclose both of them must necessarily dip between the closed curves from both sides. In successive isobars, the dip becomes less and less marked. In the wedge also, the successive isobars which turn back on themelves become less and less acute. The curve joining the turning points of successive isobars in a wedge should be smooth and not erratic.

As observations are taken at discrete points, the attempt to make isobars tend to streamlines would necessitate drawing isobars approximately as envelopes of the wind directions . In fact, if the wind directions were known at places recording the same pressure at a given epoch of time, the envelope is got by producing the wind directions (or tangent curves of the envelope) at various places and smoothing the resulting curves. As the wind directions and pressures are taken at fixed points one has to judge points of equal pressure and estimate the probable wind direction and speed there and draw the isobar. The isobar so drawn should not be at variance with the existing observations or the observations that may come in later. The isobar that can be drawn with greatest certainty is drawn first and the

pattern is completed round about it or making it a part of a bigger system. The distance between successive isobars (drawn at equal pressure intervals)

FIG. 1.

FIG. 2

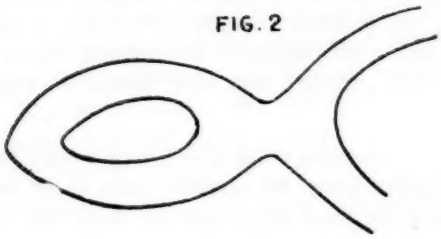
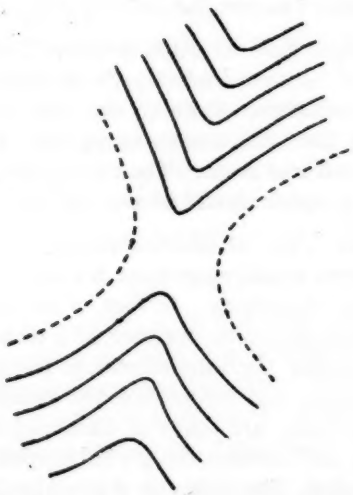


FIG. 3.



is adjusted with the help of the wind speed in that area. When an isobar bends on itself at a point, the wind speed at the point is nil (calm). Over

a chart covering a wide area, each small area is completed and extended to the next area to form a logical picture. To take the extreme case, examples

FIG. 4.

FIG. 5.

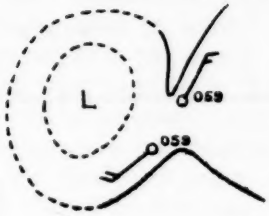


FIG. 6.

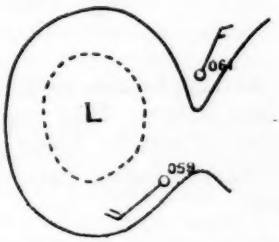


FIG. 7

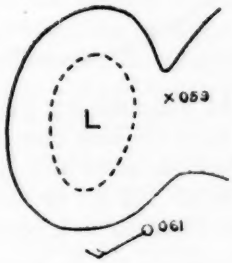
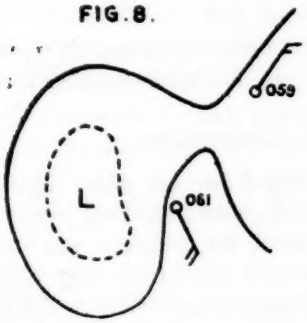


FIG. 8.



PRESSURES PLOTTED
IN TENTHS OF MILLIBARS.
(*Hundreds & Thousands Figures omitted*)

WINDS PLOTTED IN
TERMS ½ FEATHERS

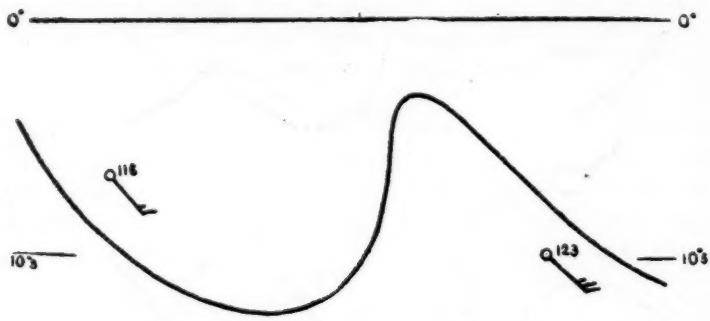
FIGS. 4-8 REFER TO
NORTHERN HEMISPHERE

of isobar drawing at the boundary of one's observations are given with two observations:

The concepts inherent in the examples are necessary in storm warning work and must have been used by many workers. But they can be used daily in drawing weather charts at the boundaries of one's observations,

particularly in the Persian Gulf, Arabia and the South Indian Ocean from where the number of observations received are very small. How sharp the various kinks or dips should be depends on the individual forecaster and the relative importance he attaches to the kink. When he expects that the

FIG. 9.



air mass is to be indicated and partitions marked, he may make the kink prominent and carry the kink over in successive isobars. If by chance more observations from the same area are recieved, it will be found that the pattern of the isobar will not be materially changed though particular lines may have to be displaced to a certain extent.

A logical sequence in the isobaric pattern should be maintained in successive synoptic charts.

As far as possible, the observations from stations of poorly represented areas should be given full weight so that no essential weather feature is missed.

Methods used in Drawing Conclusions

The meteorological observation received from the wide region were used almost immediately for daily forecasting and little time was spent to collect a number of instances before a particular criterion was "verified and statistics collected". As the observations poured in they were used and any flaws in judgement corrected in the next synoptic hour. The general principles were: (1) a "confusion" of cause and effect, and the (2) the "principle of superposition."*

* The methods were outlined in a draft of Forecasting in and near India prepared in Feb.–March 1943 extracts from which were printed in Tech. Note. No. 1, 1943 of India Met. Dept.

"Confusion" of cause and effect is essentially a process of looking out for similar causes when the effects are very similar. For example, when conditions are unsettled or depression is formed in the Arabian Sea during the month of October, the hot desert winds from Rajputana give very hot days over lower Sind. It would therefore be natural to look out for unsettled conditions or even a depression in the month of October if the temperatures are abnormally high over lower Sind. This method is one of probability and not necessarily one of certainty. It is necessary to stress this point, as it may be argued that there are several instances in October, when temperatures were high over Sind and there was no trace of a depression in the Arabian Sea. Taking another example, when the upper winds at 2 and 3 kms. at Lahore are southerly in winter, rain falls subsequently in Kashmir. The fact that there are occasions when winds were favourable for rain in Kashmir without any subsequent precipitation does not take away the utility of the criterion evolved from experience. It is possible to magnify the differences between the weather charts and argue that no two charts are alike. It is more profitable to confine oneself to those aspects of the problem which can be solved and systematised and leave the finer details for later study. The broad common features will then be evident.

"Principle of superposition", the weather at a place is due to the combined effect of the prevalent circulation and any perturbing factor. The method of obtaining the resultant depends on the particular problem and on the relative magnitudes of the prevailing circulation and the perturbing factor. The land and sea breezes are minor perturbations on the general circulation, while the S.W. monsoon is a major perturbation on the circulation of the atmosphere in the tropics. The monsoon depressions are perturbations imposed on the S.W. monsoon.

The method of cause and effect comes in even in drawing isopleths or fronts or partitions. The lines representing these are drawn with a view to account for the weather actually experienced. For a novice, it is puzzling that, after having drawn a front or partition or even a wedge by taking account of the actual weather, the same front or partition or even a wedge is given as a reason for the weather. The process employed has a good logical background. It corresponds to the successive approximations of an equation or to the self-consistent models in atomic physics. Just as the case of an atom, after final evaluation, the density of electrons and the field strength should be consistent with each other, and as in the case of an equation the final root should satisfy the original equation for which successive approximations were sought, the weather and the picture of isobars, partitions, fronts or wedges must all be self-consistent.

In the method of drawing isobars outlined above, it is often noticed that a number of small low pressure areas will have been drawn. Every one of them will not be a depression or even give rise to one. But at the same time they are not altogether to be ignored. Some of the low pressure areas are quasi-permanent with only a small shift in their locality and intensity from day to day.* Others move in a more or less regular fashion. The motion of monsoon "pulses" have been shown to be associated with the movement of shallow low pressure areas from south of the equator to the north (*ibid.*). The movement of far-eastern transitional air is also often associated with the motion of shallow low pressure areas. It is likely that even at other places, the motion of shallow low pressure areas should exist when maritime air is involved but is masked due to steeper pressure gradients there. The motion of dry continental air is however shown by the steeper pressure gradients, which one would associate with the rear of extra-tropical depressions. The significance of the quasi-permanent and moving low pressure areas have been given in the book. Usually the low pressure areas arrange themselves in a systematic fashion in the Indian area. When there are more closed isobars or steeper pressure gradient (in the afternoon) than usual more instability weather can be expected. A natural inference of the existence of the shallow lows and absence of weather on many occasions would be that, these shallow low pressure areas indicate a certain amount of vorticity in the isobaric system and if energy is fed into them by incursion of maritime air (or more southerly air in the northern hemisphere) weather often results. In other words, two distinct features; vorticity and injection of a maritime air (a northward flow of air in the northern hemisphere) are both required to produce weather. These points are being looked into further.

Summary

The subject of Tropical Meteorology is of late assuming importance to be dealt with theoretically. Meteorological network is also being developed. It is shown that even in the tropics, in the region of steady winds and small pressure gradients, the isobars follow the wind directions. Taking the idea of streamlines and isobars at upper levels in higher latitudes, methods of drawing isobars are given. This is particularly important, as due to small pressure gradients in the tropics, there is great latitude in drawing isobars and some almost ignore the pressure values. Methods of drawing conclusions from meteorological facts are given.

* Tech. Note. No. 20, India Met. Dept. 1945 and also p. 13 of "Forecasting Weather and near India" released Nov, 1945 to be re-printed later with diagrams, tables and addend:.

A SIMPLE NOMOGRAM FOR THE RATE OF ASCENT OF RUBBER BALLOONS AND IMPROVED TECHNIQUE WITH BALLOONS AND BALLOON MATERIAL*

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Received March 3, 1947

NOMOGRAM

THE rate of ascent of a rubber balloon filled with a lighter gas is very important for the meteorologists as they have to send up many rubber balloons daily for their work. The rubber balloons are usually filled with hydrogen and let off to determine the upper winds (pilot balloon) or to study the temperature structure of the upper air (sounding balloons—like radio sonde, etc.). By triangulating the positions of a pilot balloon, either by using two theodolites or by using the well-known tail method, the direction and speed of the upper air is determined. But the time taken for the calculation of the winds after the balloon is let off is more than what the customers of upper-air-aviators and weather forecasters—would allow. Time-saving methods are introduced and simplifications have to be made. The uniform rate of ascent method does away with the necessity of finding the height co-ordinate of the balloon and the method is used in most countries where the effect of convection is not large enough to vitiate the results. To secure uniform rate of ascent the amount of hydrogen that fills the balloon is determined. In any lot of balloons even from the same works, the weight of balloons varies so much individually that it is not possible to give the same amount of gas or give the same free-lift to the balloon. Tables have to be constructed so that the free-lift of the balloon can be determined from the rate of ascent and the dead-weight of the balloon. The formula used is

$$R = kL^{\frac{1}{2}}/(L + W)^{\frac{1}{2}}$$

where R is the rate of ascent of the balloon, k is a constant, W is the dead-weight of the balloon and L is the free-lift of the inflated balloon.

The Americans (U.S.A.) use practically the same formula except that instead of R, $R^{1/m}$ is used where m is another constant which is nearly unity.

The equation consists of three variables and the first impression is that a number of graphs are required connecting the rate of ascent, the weight

* The work was done in 1935–36 when I was in Upper Air-Observatory, Agra.

and the free-lift of the balloons. Some have actually constructed many graphs. But even then, the disadvantage is, that if for some reason the rate of ascent or the value of the constant has to be changed, a series of new graphs will be required to be drawn. If the work can be simplified it would greatly add to the elegance and saving of avoidable work.

If in the above equation L is replaced by $(R/k)^4$ Y and W is replaced by $(R/k)^4$ X in the usual formula;

or if L and W are replaced by $(R/k)^{4/m}$ Y and $(R/k)^{4/m}$ X in the U.S.A. formula, the equations for the rate of ascent would be all reduced to a single simple formula

$$Y^3 = (Y + X)^3$$

This is an elementary equation whose graph can be constructed with the help of square and cube tables. Reading off from it could be made easy by taking an open scale. Whatever changes may be introduced in the rate of ascent, or the constants involved in the formula, the equation is unaffected, and hence the construction of a large number of graphs is rendered superfluous. The construction of the graph with suitable co-ordinates takes hardly a few minutes and the tables for any given rate of ascent take only an hour for a usual range of weight of balloons in any category. The only change that is introduced by a change in the constants or in the rate of ascent is the factor which multiplies both Y and X to give the free lift and dead weight.

Weight of Attachments to a Balloon

In a formula the dead weight of the balloon W is considered. The formula is partly empirical and partly based on general principles, of the resistance to a moving expanding sphere. At the time of discussion the question of attachments does not arise. In some countries, like England, the weight of the attachments is added to the dead-weight of the balloon before the rate of ascent is determined. In other countries notably Germany (and India before 1938) the weight of attachments is compensated by an additional free-lift equal to it. An experimental verification is hardly possible without bringing in other unknown factors. The correct procedure is probably somewhere between the two methods.

$(L + W)^{\frac{1}{3}}$ is proportional to the diameter of the inflated balloon (see below) and adding the weight of attachments to the dead-weight of the balloon means a virtual increase in the size of the sphere considered. The increase in the size of the sphere brings in more friction and surface resistance. If the weight of the attachment is compensated by an addition to

the free-lift, there is no addition to the superficial resistance, contemplated. The free lift formula is really due to balancing of forces, one due to the surface resistance and the other rise due to buoyancy. If the weight of the attachments are not unduly large compared with the dead weight of the balloon, the fact that the nomogram involves a factor $(R/k)^6$ for the free-lift or the dead weight; the difference in the rates of ascent by using the alternative methods regarding the weight of the attachments is really small. In most cases it does not exceed 2·5% which is below the accuracy of our measurements.

Balloon Technique

Though a meteorologist is primarily interested in the finished rubber balloons and the upper air observations, he must be able to distinguish different consignments of balloons that he gets and utilise them most economically. The balloons made by different factories vary in size, weight, quality and consistency. Even from the same manufacturer different consignments show different results. It is not immediately necessary to go into theoretical considerations why it is so. It is sufficient if workable ideas can be put together.

Rubber balloons were obtained from various sources. Cold vulcanised rubber sheetings were also got and balloons made out of them by pasting sectors with suitable adhesives locally. A quantitative comparison of their performance and deterioration of the balloon stock would add to efficiency of work. To wait for fine weather, and let off and determine how high the balloon went was definitely unsatisfactory. For a long time there was a practice of testing a few balloons of each stock by inflating them to destruction and noting the destruction diameter. A systematisation involving simple ideas was therefore adopted.

1. In the earlier years when the type of balloon was variable, it was customary to measure the dead weight of the balloon, the diameter of the inflated balloon on the ground and also the free-lift. As the quality of the balloons had become uniform and practically spherical on inflation, the measurements of all the three quantities were unnecessary, because of the formula

$$(L + W) = \frac{13{\cdot}85 \times 1{\cdot}293 \times 273 \times \pi \times d^3}{14{\cdot}85 \times (273 + \theta) \times 6}$$

Where θ is the temperature in degrees Centigrade, d the inflated diameter measured in metres, and the free-lift and dead weight and W are given in kilograms. The volume of hydrogen gas that is required to fill the balloon at temperature θ and the atmospheric pressure is

$$0{\cdot}83\,(273 + \theta) \times (L + W)/273 \text{ in cubic metres.}$$

2. *Test of Efficiency.*—The main reason of using rubber for balloons is its power of stretching. The thinner, the rubber sheeting of the balloon can be stretched without tearing, the better is its quality. The surface area of an inflated balloon can easily be calculated and this multiplied by the thickness of the sheeting and the density gives the weight of the balloon. In the spherical balloons the measurement of the diameter is sufficient. The bursting diameter may be denoted by D. If different rubber materials had the same efficiency they would tear when the same thickness is attained after stretching. As the density of the rubber is fairly constant, the thinness is given by the weight of the balloon divided by the surface area except for the density factor. In the spherical balloons of the same efficiency, the ratio

$$D^2/W \text{ must be constant.}$$

Hence it is worthwhile noting the quantity

$$E = 6{\cdot}25\, D/W^{\frac{1}{2}} \quad (D \text{ in metres})$$

The constant 6·25, which is a submultiple of 100 was taken as the best balloons gave a value of 100 for the above factor. Others hardly touched 90, and E becomes a sort of percentage efficiency factor.

In a given sample of balloons, two or three were burst to destruction and the mean value taken as D. If the individual values differed widely, more balloons were burst to get at the mean value. The spread of the individual efficiency factors also represents the uniformity of reliability of the balloon consignment. When sheetings had to be tested, small balloons of 6·0″ diameter (uninflated) were made and tested to destruction. Making small sample balloons saved a good amount of material. The variation in efficiency factor with time of balloons stored under different conditions gave an idea of the decay of the balloon material. Various material could be quantitatively compared.

3. *Height attained by the ascending balloon.**—The next important question that arises is the height upto which the balloon may be expected to rise. Given the efficiency of the particular rubber material, given by the tests of the last paragraph, and the weight of the balloon, it is possible to compute the bursting diameter of the balloon. It may be assumed that that the balloon actually bursts at this diameter. If d is the diameter on the ground of the inflated balloon and D is the bursting diameter, θ is the ground temperature, and θ_h the temperature at the bursting height, when there is no leakage of gas we have

$$d/(273 + \theta)^{\frac{1}{3}} = D/(273 + \theta_h)^{\frac{1}{3}}$$

* See also an article by L. H. G. Dines. Met. mag.—vol. 64, p. 57, 1929.

Hence to a first approximation, the balloon may be expected to burst at a height where the pressure is given by

$$1000\,(d/D)^3 \times (273 + \theta_h)/(273 + \theta) \text{ millibars}$$

The reason for saying as a first approximation is that there are many unknown factors which might change the level of bursting, the efficiency of the rubber sheet may change at the low temperatures above, the balloon may not expand till the maximum is reached and the convection currents and local heating of the balloon may carry it far higher than indicated by the formula. But as a working model it is as satisfactory as any.

The importance of the above formula is that one can determine the type of balloon that is to be used for various types of ascents. If high pilot balloon winds are required an approximate calculation would show whether a particular type of balloon is capable of attaining the height or not. Among those that can attain the height, and to safeguard accidents a couple of kilometres more, the most economical balloon can be chosen, *i.e.*, unnecessarily large balloons can be saved up. Another important use is that if a sounding balloon has to be recovered to work out the record as in Dines meteorograph in a region where the balloon would be carried off if it attained great heights, the free lift can be adjusted so that the balloon would burst at a predetermined height which ensures recovery. In N.W. India balloons were let off to burst at about 12–13 kms. for facility of recovery in 1936. It is only necessary to see that in the formula for the height attained, the pressure for about 12 kms. (average pressure estimated at that height) is taken to be that for the bursting height. It may be pointed out that fuses do not operate at such great heights.

The formula yields another result. For the same type of balloon material (with the same efficiency) D is prportional to $W^{\frac{1}{3}}$ and d is proportional to $(L + W)^{1/3}$. Hence $(d/D)^3$ is proportional to $(L + W)/W^{3/2}$; or if the free-lift and the dead weight of the balloon are taken to be of the same order $(d/D)^3$ is proportional to $1/W^{\frac{1}{2}}$ and hence to $1/d^6$. Hence it follows that it is the one-sixth power of the diameter that determines the height to which a balloon will attain. This leads to the conclusion that by a small increase in the size of a balloon, there is not much advantage gained and conversely to increase the height attained by a balloon even by a small height the increase required in the diameter of the balloon is disproportionately large. A large balloon is costly for gas also. If on the other hand the efficiency of the balloon material could be increased, there would be a good chance of attaining greater heights. As a result of this the size of the balloon can be decreased till it is able to "just not function" with its attachments

like the sounding balloon equipment. In practice, a liberal allowance is always made, in the size of the balloon.

4. *Shape of the balloon.*—In an inflated rubber balloon, if r and r' are the two radii of curvature, dp is the difference of pressure inside and outside the balloon and T is the superficial strength of the rubber sheeting

$$1/r + 1/r' = dp/T$$

the usual surface tension formula.

The only surface that keeps at all its points constant total curvature and continues to keep constant (though the actual constant may vary) curvature at every stage of expansion is a sphere. If there be unequal value of the total curvature of the rubber balloon due to non-uniformity of material or due to its construction with non-spherical sectors, the thickness of the rubber material varies at various points of the surface. There would be a preferential tendency for the balloon material to give way at its thinner point. This effect will be magnified as the balloon ascends and the balloon may not attain the heights attained by spherical balloons. It follows therefore that the rubber balloons are most efficient when they are initially spherical and continue to remain spherical at all stages of expansion, *i.e.*, stretch uniformly.

5. *Cementing of Cellophane material.*—Attempts were also made to make balloons from various tissues which are non-expansible. Field* has described fully the making of gutta-percha balloons. With Cellophane sheetings (which are light and better preservable than gutta-percha) the ordinary adhesives would not give a gas-tight joint. After several tests, it was found that if a narrow strip of gutta-percha is kept between two overlapping edges of cellophane sheetings and a hot iron (just heated to about 150° C) is passed over the edge, the joint becomes gas tight and balloons can be made of the material. The joint is further moisture-proof. This cementing may have applications in other fields also.

SUMMARY

The formula for the rate of ascent of a rubber balloon filled with a lighter gas contains two other variables, the dead weight of the balloon and the free-lift of the inflated balloon. Usually many graphs have to be drawn connecting the three variables for use. By a simple transformation it is shown that all the formulæ are reduced to $Y^3 = (Y + X)^2$ which can be

* Field. Memoirs of Ind. Met. Dept., vol. 24, p. 133.

graphed easily. The importance of this formula is explained by showing that there is little actual difference in the rate of ascent whether the weight of attachments are added to the dead-weight of the balloon or subtracted from the free-lift before applying the formula.

To utilise balloons economically and predetermine their behaviour in practice, it is necessary to make comparisons quantitatively. Simple formulæ are given.

A method of pasting two sheets of cellophane material is given which leads to a gas-tight and moisture-proof joint.

CONGRUENCE PROPERTIES OF σ_a (N)

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§ 1. Introduction

The object of this paper is to investigate completely the congruence properties of $\sigma_a(N)$,[1] the sum of the 'a'th powers of the divisors of the positive integer N. The two fundamentals theorems of this theory were announced by me,[2] recently in the 'Mathematics Student'. They are

Theorem A.—If $k > 2$, $(k, l) = 1$ then a necessary condition that $\sigma_a(km + l) \equiv 0 \pmod{k}$ for every $m > 0$ is

$$l^a \equiv -1 \pmod{k} \tag{1}$$

Theorem B.—If $k > 2$, $(k, l) = 1$ and $l^a \equiv -1 \pmod{k}$ then a necessary and sufficient condition that $\sigma_a(km + l) \equiv 0 \pmod{k}$ for every $m > 0$ is

$$x^{2a} \equiv 1 \pmod{k} \tag{2}$$

for every x prime to k.

Thus the problem of congruence properties of $\sigma_a(N)$ is solved if we are able to solve the two binomial congruences

$$l^a \equiv -1 \pmod{k}$$
$$x^{2a} \equiv 1 \pmod{k}$$

for every x prime to k.

These congruences of $\sigma_a(N)$ have not, as far as I know, been noticed before in mathematical literature. Mr. Hansraj Gupta,[3] to whom these results were communicated, has published proofs of these. Here I show that these results are natural consequences of Dirichlet's theorem on the infinitude of primes in an arithmetical progression.

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* The Contents of this paper formed part of a M.Sc. thesis of the Madras University (1946).

[1] The arguments of the paper hold good even if N is negative provided we define $\sigma_a(N)$ as $\frac{1}{2} \sum_{\delta | N} \left| \delta^a + \left(\frac{N}{\delta}\right)^a \right|$; 'a' may be also negative and then $\sigma_a(N) = N^{-a}\, \sigma_{-a}(N)$.

[2] *Mathematics Student*, 1945.

[3] *Mathematics Student*, 1945.

It is shown in the sequel that the moduli k for which congruences of $\sigma_a(N)$ exist belong to a set of numbers called by me, sigma numbers. Also if k is a sigma number it is shown that 'a' has a least value $\frac{1}{2}\lambda$ all the other values of 'a' being got by multiplying this least value by an odd number. The converse problem of determining the value of k when 'a' is given is difficult. I give in this paper only some empirical solutions of this problem reserving detailed discussions for a future occasion.

I wish to express my thanks to Dr. Vaidyanathaswamy, Reader in Mathematics, Madras University, for his help in the preparation of this paper.

§2. On the Group R (k)

We shall begin by deriving some simple results in the theory of the group $\mathbf{R}(k)$ of prime residue classes mod k.

With Hecke[4] we shall call this group $\mathbf{R}(k)$. It is well known that if p is an odd prime and α is any integer greater than zero then $\mathbf{R}(p^\alpha)$ is cyclic; $\mathbf{R}(2^\alpha)$ is cyclic if $\alpha = 1$ or 2 but if $\alpha \geqslant 3$ then it is a direct product of two cyclic groups of orders 2 and $2^{\alpha-2}$ represented respectively by $(1, -1) \pmod{2^\alpha}$ and $(1, 5, 5^2, \ldots) \pmod{2^\alpha}$. If $k = 2^\alpha p_1^{\alpha_1} \ldots p_r^{\alpha_r}$ then $\mathbf{R}(k)$ itself is the direct product of $\mathbf{R}(2^\alpha)$, $\mathbf{R}(p_1^{\alpha_1}) \ldots \mathbf{R}(p_r^{\alpha_r})$. The exponent[5] of $\mathbf{R}(k)$ is the least common multiple (l.c.m.) of the orders of all elements of $\mathbf{R}(k)$ and it is equal to $\lambda = \lambda(k)$ where

$$\begin{aligned} \lambda(k) &= \text{l.c.m. } [2, 2^{\alpha-2}, \phi(p_1^{\alpha_1}), \ldots \varphi(p_r^{\alpha_r})] && \text{if } \alpha \geqslant 3 \\ &= \text{l.c.m. } [\varphi(p_1^{\alpha_1}), \ldots \phi(p_r^{\alpha_r})] && \text{if } \alpha \leqslant 2 \end{aligned} \tag{3}$$

where $\phi(n)$ is Euler's totient function.

From the definition of exponent it is evident that λ is the least value of y such that

$$x^y \equiv 1 \pmod{k}$$

for every x in $\mathbf{R}(k)$ *i.e.*, every x prime to k.

Consider now the congruence

$$x^{\frac{\lambda}{2}} \equiv -1 \pmod{k}. \tag{4}$$

This implies the congruences

$$x^{\frac{\lambda}{2}} \equiv -1 \pmod{2^\alpha} \tag{5}$$

$$\equiv -1 \pmod{p_t^{\alpha_t}} \quad (t = 1, \ldots r) \tag{6}$$

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[4] E. Hecke. *Theorie der Algebraischen Zahlen*, Leipzig, p. 51 *et seq.*

[5] A. A. Albert. *Modern Higher Algebra*, p. 130.

The congruences (6) can be satisfied if and only if $\frac{\lambda}{2}$ is an odd multiple of $\phi(p_1^{a_1})$, $\phi(p_2^{a_2})$,.... which means that p_1-1. p_2-1,.... must all contain the same even elementary block factor.[6] We shall call such primes p similar primes. Taking (5) we see that $\frac{\lambda}{2}$ must be odd and $x \equiv -1 \pmod 2$. Further since $\frac{\lambda}{2}$ involves $\phi(p_1^{a_1})$....etc., we see that if $a \geqslant 2$ then $a \leqslant 3$ and all the odd prime factors of k must be of the form $4n-1$. Hence the important

THEOREM 1.—The necessary and sufficient condition that the congruence

$$x^{\frac{\lambda}{2}} \equiv -1 \pmod k$$

is solvable is

(i) If k is odd or twice an odd number then all the odd prime factors of k are similar.

(ii) If k is divisible by 4 then it should not be divisible by 16 and all the odd prime factors of k must be of the form $4n-1$.

We shall call these numbers, the 'sigma numbers'. It is seen that any solution of the congruence when it exists is of the form

$$\begin{aligned} x &\equiv t_s \pmod{p_s^{a_s}} \ (s = 1, \ldots . r) \\ &\equiv -1 \pmod{2^a} \end{aligned}$$

where t_s is any quadric non-residue (mod $p_s^{a_s}$). The number of solution is thus $\frac{\phi(k)}{2^t}$ where[7]

$$\begin{aligned} t &= r \text{ if } a = 0 \text{ or } 1 \\ &= r+1 \text{ if } a = 2 \\ &= r+2 \text{ if } a > 3. \end{aligned}$$

k being equal to $2^a p_1^{a_1} \ldots . p_r^{a_r}$.

§ 3. PARITY OF $\sigma_a(N)$

Before proving the fundamental theorems A and B we shall consider the parity of $\sigma_a(N)$ *i.e.*, the oddness or evenness of $\sigma_a(N)$. We shall also prove some simple elementary congruences of $\sigma_a(N)$.

THEOREM 2.—$\sigma_a(N) \equiv 1 \pmod 2$ (7)

if and only if the complete odd block factor of N is a perfect square.

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[6] b is a block factor of N if $\left(b, \frac{N}{b}\right) = 1$. It is an elementary block factor if it is a prime power.

[7] H. Weber, *Lehrbuch der Algebra*, Bd. 2, I Chapter.

Proof.—

$$\sigma_a(N) = \sum_{\delta/N} \delta^a \equiv \sum_{\substack{\delta/N \\ \delta \text{ odd}}} 1 \pmod 2$$

Thus $\sigma_a(N)$ has the same parity as the number of odd divisors of N. But if $N = 2^{\alpha} p_1^{\alpha_1} \ldots p_r^{\alpha_r}$ then the number of odd divisors of N is $(1+\alpha_1)(1+\alpha_2)\ldots(1+\alpha_r)$. This is odd if and only if $\frac{N}{2^{\alpha}}$ is a perfect square.

Since $x^{\lambda} \equiv 1 \pmod k$ for every x prime to k we easily deduce that

$$\sigma_a(N) \equiv \sigma_b(N) \pmod k \qquad (k, N) = 1 \tag{8}$$

if $a \equiv b \pmod \lambda$.

In particular if $b = 0$ then

$$\sigma_{\lambda}(N) \equiv d(N) \pmod k. \qquad (N, k) = 1 \tag{9}$$

$d(N)$ being the number of divisors of N.

§ 4. Proof of Theorems A and B

We shall make use of the following theorem of Dirichlet in proving our theorems.

Dirichlet's theorem.—If $l < k$ and $(k, l) = 1$ then there are an infinity of values of m for which $km + l$ is a prime number.

Proof of theorem A.—Consider the series of numbers $l, k+l, 2k+l, \ldots$ and the corresponding series of numbers $\sigma_a(l), \sigma_a(k+l), \ldots$. If all the numbers of the second series are divisible by k then whenever $km+l$ is a prime, $\sigma_a(km+l)$ is also divisible by k. For then

$$\sigma_a(km+l) = 1 + (km+l)^a \equiv 1 + l^a \equiv 0 \pmod k.^{8}$$

Proof of theorem B.—To prove this we require the following:

Lemma.—If $k > 2$, $(k, l) = 1$, $l^a \equiv -1 \pmod k$ and $x^{2a} \equiv 1 \pmod k$ for every x prime to k then $km+l$ is not a perfect square for any value of $m > 0$.

For if δ and δ^1 be two conjugate divisors of $km+l$ then $\delta\delta^1 \equiv l \pmod k$ and

$$(\delta\delta^1)^a = l^a \equiv -1 \pmod k$$

But if $\delta = \delta^1$ then $1 \equiv \delta^{2a} \equiv (\delta\delta^1)^a \equiv l^a \equiv -1 \pmod k$ which is absurd since $k > 2$.

We shall now prove theorem B.

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[8] This Condition though necessary is not sufficient. For if $k = 35$ and $a = 3$ then $l^3 \equiv -1 \pmod{35}$ has solutions 19, 24, 34. $\sigma_3(3\cdot 35 + 19)$, $\sigma_3(2\cdot 35 + 24)$, $\sigma_3(35+34) \not\equiv 0 \pmod{35}$.

The condition is sufficient. For if δ and δ^1 be any two conjugate divisors of $km+l$ then

$$\delta^a(\delta^a+\delta^{1a}) = \delta^{2a}+(\delta\delta^1)^a \equiv 0 \pmod{k}$$

Thus $\delta^a+\delta^{1a} \equiv 0 \pmod{k}$ for every two conjugate divisors of $km+l$ and $km+l$ has an even number of divisors.

The condition is necessary.

Let us choose a prime p not dividing k. Then there is a prime q (in fact an infinity of them) such that

$$pq \equiv l \pmod{k}.$$

Now let $\sigma_a(pq) \equiv 0 \pmod{k}$. Then

$$\sigma_a(pq) = (1+p^a)(1+q^a) = 1+p^a+q^a+(pq)^a$$
$$\equiv p^a+q^a \pmod{k}.$$

Multiplying by p^a which does not divide k, we get

$$p^{2a} \equiv 1 \pmod{k}$$

But p is any prime not dividing k and in every prime residue class there are an infinity of such primes. Thus the necessity of the condition.

Thus the theory of congruences of $\sigma_a(N)$ is reduced to a study of the binomial congruences

$$l^a \equiv -1 \pmod{k} \tag{10}$$

$$x^{2a} \equiv 1 \pmod{k} \tag{11}$$

for every x prime to k.

§ 5. Solution of the Congruences

From (11) it is evident that $2a$ must be a multiple of $\lambda = \lambda(k)$, the exponent of the group of prime residue classes mod k. Let $2a = s\cdot\lambda$ where s is an integer. Then (10) shows that s is an odd number. Now $k > 2$ and hence λ is even and greater than 1. Let $s = 2b+1$. Then

$$-1 \equiv l^{\frac{(2b+1)\lambda}{2}} = l^{b\lambda}\cdot l^{\frac{\lambda}{2}} \equiv l^{\frac{\lambda}{2}} \pmod{k}.$$

so that (10) implies the congruence $l^{\frac{\lambda}{2}} \equiv -1 \pmod{k}$.

The least value of 'a' is thus $\frac{\lambda}{2}$ and k is a sigma number. Thus

Theorem 3.—If $\sigma_a(km+l) \equiv 0 \pmod{k}$ for $(k, l) = 1$ then

(i) k is a sigma number

(ii) 'a' is an odd multiple of $\frac{\lambda}{2}$.

It may be remarked that Mr. Hansraj Gupta in his paper does not get all the values of k and arrives at the wrong conclusion that k cannot contain odd prime factors of the form $4n+1$. We shall give some examples illustrating the above theory.

(i) $k = 3 \cdot 7 = 21$. $\lambda(21) = 6$. Solutions of $l^3 \equiv -1 \pmod{21}$ are 5, 17, 20. Thus $m \geqslant 0$.

$\sigma_3(21m+5)$, $\sigma_3(21m+17)$, $\sigma_3(21m+20) \equiv 0 \pmod{21}$.

(ii) $k = 2^3 \cdot 7 = 56$. $\lambda(56) = 6$. Solutions of $l^3 \equiv -1 \pmod{56}$ are 31,47,55.

$\sigma_3(56m+31)$, $\sigma_3(56m+47)$, $\sigma_3(56m+55) \equiv 0 \pmod{56}$.

§ 6. Determination of k when 'a' is given

We have so far been concerned with the determination of 'a' and 'l' when k is given. We shall now take the converse problem. Given 'a' what are the congruences or what are the possible values of k. It was observed that k is a sigma number; also 'a' is an odd multiple of $\frac{\lambda}{2}$ so that $2a$ is an odd multiple of λ. Let us denote by $N(t)$ the number of solutions[9] in sigma numbers of

$$t = \lambda(x)$$

then it is easily seen that the number of k's for a given 'a' is given by

$$\Sigma N\left(\frac{2a}{\delta}\right)$$

where δ runs through all odd divisors of $2a$. The solution of this problem is very difficult. But if 2^α is the even elementary block factor of $2a$ then each one of the prime factors of k must be such that $p-1$ contains 2^α as the even elementary block factor. Let us take some important examples.

(i) Let a be an odd number. Then the number of values of k is

$$\sum_{\delta \mid a} N\left(\frac{2a}{\delta}\right)$$

If $a = 15$ then solutions in sigma numbers should be found of

$2 = \lambda(x)$, $6 = \lambda(x)$, $10 = \lambda(x)$, $30 = \lambda(x)$.

The solutions are

3	$7 \cdot 11$	$3 \cdot 7 \cdot 31$
7	$7 \cdot 31$	$7 \cdot 11 \cdot 31$
11	$11 \cdot 31$	$3^2 \cdot 7 \cdot 11$

[9] For solution of similar Problems see another paper by the author.

31	$3^2 \cdot 31$	$3^2 \cdot 11 \cdot 31$
3^2	$3^2 \cdot 11$	$3^2 \cdot 7 \cdot 31$
$3 \cdot 7$	$3^2 \cdot 7$	$3 \cdot 7 \cdot 11 \cdot 31$
$3 \cdot 11$	$3 \cdot 7 \cdot 11$	$3^2 \cdot 7 \cdot 11 \cdot 31$
$3 \cdot 31$	$3 \cdot 11 \cdot 31$	

together with these multiplied by 2, 4 and 8. Also 4 and 8 are solutions so that there are 94 solutions.

(ii) Let $a = 2^a$; since this cannot be an odd multiple of any number we must find a sigma number k such that $\lambda(k) = 2^{a+1}$. This means that $2^{a+1} + 1$ is a prime number. Obviously this must be a Fermat prime.

(iii) Let $S(a)$ denote the set of numbers k for which congruence properties of $\sigma_a(N)$ with k as modulus exist. If 'a' is odd and b any divisor of 'a' then

$$S(b) \subset S(a)$$

Since unity divides every odd number

$$S(1) \subset S(a).$$

Thus the set $S(1)$ consists of sigma numbers k for which congruence properties of $\sigma_a(N)$ exist whatever odd number k is. We now prove the

THEOREM 4.—The set S (1) consists of the numbers 3, 4, 6, 8, 12 and 24 only.

Proof.—The only solutions of $\lambda(x) = 2$ are $x = 3, 4, 6, 8, 12$ and 24.

In this case there is only one value of l namely $-1 \pmod k$ so that we have the

THEOREM 5[10].—If $k = 3, 4, 6, 8, 12$ or 24 then

$$\sigma_a(km - 1) \equiv 0 \pmod k, \quad m > 70 \tag{13}$$

whatever odd number k is.

A companion to this theorem would be.

THEOREM 6.—If $(n, k) = 1$ and $k = 3, 4, 6, 8, 12$ or 24 then

$$\sigma_a(n) \equiv d(n) \pmod k \tag{14}$$

$d(n)$ being the number of divisors of n and 'a' any even number.

§7. We have so far been concerned with congruences of the type $\sigma_a(km + l) \equiv 0 \pmod k$, $(k, l) > 1$. We shall now prove the

Theorem.—If $(k, l) = 1$ and $g > 0$ there are no values of k for which

$$\sigma_a(km + l) \equiv g \pmod k \tag{15}$$

for every $m > 0$.

---

[10] K. G. Ramanathan, *Mathematics Student*, 1943, 33–35.

Proof.—It is evident from the proof of theorem A that

$$l^a \equiv g - 1 \pmod{k}.$$

Let us choose two primes p and q not dividing g such that

$$pq \equiv l \pmod{k}.$$

Then $\sigma_a(pq) \equiv g \pmod{k}$ implies

$$g \equiv 1 + p^a + q^a + (pq)^a \pmod{k}.$$

showing that $p^a + q^a \equiv 0 \pmod{k}$.

Multiplying by p^a which does not divide k we get

$$p^{2a} \equiv 1 - g \pmod{k}. \tag{16}$$

It is easily seen from the group property of the residue classes as well as Dirichlet's theorem that this congruence cannot hold good unless $g = 0$.

§. In this last article I shall state a congruence property of Ramanujan's function $\tau(n)$.[11] Proof is published elsewhere.[12]

Ramanujan's function $\tau(n)$ is defined by

$$\sum_{n=1}^{\infty} \tau(n)\, x^n = x\,[(1-x)(1-x^2)\ldots.]^{24} \tag{17}$$

THEOREM 8[13].—$\tau(n) \equiv n\sigma_2(n) \pmod{7}$. (18)

This implies Ramanujan's congruence that

$$\tau(n) \equiv 0 \pmod{7}$$

if $n \equiv 0, 3, 5, 6 \pmod{7}$. For $\sigma_3(n) \equiv 0 \pmod{7}$ if n is a quadratic non-residue of 7. More generally

THEOREM 9.—$\sigma_{\frac{p-1}{2}}(n) \equiv 0 \pmod{p}$ (19)

if n is a quadratic non-residue of the odd prime p. This is a particular case of

THEOREM 10.—If $p \nmid n$ then $\sigma_{\frac{p-1}{2}}(n) \equiv \sum_{\delta \mid n} \left(\frac{\delta}{p}\right) \pmod{p} \sum_{p \mid \delta}$ (20)

$\left(\frac{\delta}{p}\right)$ being the Legendres-quadratic residue symbol.

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[11] See G. H. Hardy, '*Ramanujan*,' Cambridge, 1940, p. 169. Ramanujan has stated such congruences only for the moduli 5 and 691, *viz.*,

$$\tau(n) \equiv n\sigma(n) \pmod{5}$$
$$\tau(n) \equiv \sigma_{11}(n) \pmod{691}.$$

[12] Proofs of theorems 8, 9 and 10 can be found in my Paper to be published in the *Journal of the Indian Mathematical Society*, 1945.

[13] Theorem 8 is substantially equivalent to theorem 1 of J. R. Wilton, *Proc. Lond. Math. Soc.*, 1931, p. 1–11.

THE PREPARATION AND PROPERTIES OF 4-PHENYLACETYL-RESORCINOL AND 4-PHENYL-ACETYL-PYROGALLOL

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In course of his preparation of C-alkyl and C-alkaryl-resorcinols for the study of antiseptic action, Klarmann[1] prepared 4-phenylacetyl resorcinol by Hoesch's method.[2] We now find that the same hydroxy-ketone can be most conveniently prepared either by the application of Nencki or the Friedel Crafts Reaction. As the chemical properties of this substance do not appear to have been studied, we have examined them in detail. The ketone gave readily the 4-nitrophenyl hydrazone, 2:4-dinitrophenyl hydrazone, diacetyl and dibenzoyl derivatives. Bromination gave the mono—as well as the dibromo-derivatives, and as they were unaffected by heating with alkali solution, the halogen atoms were present in the nucleus. Nitration gave the mono-nitro-derivative while the Clemmensen reduction gave 4-B-phenylethyl resorcinol. Kostanecki acetylation gave the mixture of 7-hydroxy-2-methyl-3-phenyl-chromone and its 7-acetyl derivative, and the original ketone was obtained on its alkaline hydrolysis. It was not possible to prepare 2:4- or 4:6-di-phenylacetyl-resorcinol by the application of the Friedel-Crafts Reaction to 4-phenyl-acetyl resorcinol.

4-Phenylacetyl-pyrogallol which was prepared by the identical method behaved similarly, in most of the reactions, and its derivatives are also described.

Experimental

A. Condensation of Resorcinol with phenylacetic acid. Preparation of 4-phenyl-acetyl-resorcinol by Nencki's method.

An intimate mixture of resorcinol (20 gm.) phenyl acetic acid (30 gm.) and powdered anhydrous zinc chloride (20 gm.) was heated in an oil-bath at 120° C. for two and half hours and then poured in acidulated ice-cold water. The product was purified through alkali and crystallised from alcohol in lustrous, long needles m.p. 115–116° (depressed by resorcinol to 90° C.) (Yield = 70 per cent).

Its alcoholic solution gave red coloration with aqueous ferric chloride. It was soluble in usual organic solvents. (Found: C, 73·0; H, 5·3; Calc. for $C_{14}H_{12}O_2$; C, 73·2; H, 5·3 per cent.)

By Friedel and Crafts method.

Solutions of resorcinol (20 gm.) in nitrobenzene (60 c.c.) and of phenyl-acetyl chloride (30 gm.) in nitrobenzene (30 c.c.) were alternately added to a cooled solution of anhydrous aluminium chloride (20 gm.) in nitrobenzene (100 c.c.). The reaction mixture was kept at room temperature for 48 hours, decomposed and steam distilled. The product obtained was purified and crystallised from alcohol in long lustrous needles m.p. 115–116° C. Undepressed by 4-phenyl-acetyl-resorcinol prepared by the previous method (yield = 60 per cent).

p-*nitrophenyl hydrazone of* 4-*phenyl-acetyl-resorcinol* was prepared by heating the ketone (0·5 gm.) with *p*-nitro-phenyl hydrazine (0·5 gm.) in alcohol (30 c.c.) on water-bath under reflux for six hours. The alcoholic solution on cooling gave short, orange-red needles m.p. 220° C. (Found: N, 11·4; $C_{20}H_{17}O_4N_3$ requires N, 11·6 per cent.)

2: 4-*Dinitrophenyl hydrazone of* 4-*phenyl acetyl-resorcinol.*—A mixture of the ketone (0·5 gm.) and 2: 4-dinitrophenyl-hydrazine (0·5 gm.) dissolved in acetic acid (20 c.c.) was heated on sand-bath under reflux for six hours. The product crystallised in small, orange red needles m.p. 189-191° C. depressed by 2: 4-dinitrophenyl-hydrozine to 158° C. (Found: N, 13·4; $C_{20}H_{16}N_4O_6$ requires N, 13·7 per cent.)

1 : 3-*diacetoxy*-4-*phenyl-acetyl-resorcinol* was prepared by heating a mixture of 4-phenyl-acetyl resorcinol (1 gm.) and acetic anhydride (4 c.c.) with a drop of pyridine on sand-bath for three hours and then pouring on powdered ice. The separated solid crystallised from acetic acid in yellow, short needles m.p. 114° C., depressed by the original ketone to 77° C. Its alcoholic solution gave no coloration with ferric chloride (Found: C, 69·9; H, 4·9; $C_{18}H_{16}O5$ requires C, 69·2× H, 5·1 per cent.)

1 : 3-*Di-benzoyl*-4-*phenyl-acetyl resorcinol* was prepared by treating a solution of 4-phenyl acetyl-resorcinol (2 gm.) in sodium hydroxide (10%; 80 c.c.) with benzoyl chloride (5 c.c.) gradually with constant stirring. The separated solid crystallised from acetic acid in fine needles m.p. 95–96° C. (Found: C, 76·9; H, 4·3; $C_{28}H_{20}O_5$ requires C, 77·1; H, 4·6 per cent.)

Bromination of 4-*phenylacetyl-resorcinol with one mol. of Bromine-Preparation of* 6-*Bromo*-4-*phenylacetyl-resorcinol.*—4-phenyl acetyl resorcinol (1 gm.) was dissolved in acetic acid (20 c.c.) and bromine (0·25 c.c.) in acetic acid (10 c.c.) was added drop by drop with constant shaking. The mixture was kept at room temperature for 24 hours and then poured in ice-cold water. The yellow solid crystallised from alcohol in yellowish,

short needles m.p. 103° C. (Found : Br., 25·9; $C_{14}H_{11}O_3$. Br. requires Br. 26·1 per cent.)

Bromination with two mols. of Bromine-Preparation of 2:6-dibromo-4-phenyl acetyl-resorcinol.—A solution of bromine (0·5 c.c.) in acetic acid (10 c.c.) was gradually added to the cold solution of 4-phenyl-acetyl-resorcinol (1 gm.) in acetic acid (40 c.c.). The product obtained on keeping the reaction for 48 hours crystallised from chloroform in short, orange needles m.p. 180° C. (Found: Br., 41·0; $C_{14}H_{10}O_3$. Br_2 requires Br. 41·3 per cent.)

The mono as well as the dibromo-derivatives were unaffected by heating with 10 per cent. alkali solution.

Nitration of 4-phenyl-acetyl-resorcinol with one mol. of fuming nitric acid and preparation of 6-nitro--4-phenyl-acetyl-resorcinol.—Solution of fuming nitric acid (d = 1·5; 0·4 c.c.) in acetic acid (5 c.c.) was gradually added, with constant shaking to an ice-cold solution of 4-phenyl-acetyl-resorcinol (2 gm.) in acetic acid (30 c.c.). The reaction mixture was kept for 48 hours and then poured in water. The reddish orange solid crystallised from alcohol in small, yellow needles m.p. 156–157° C. (Found: N, 5·6; $C_{14}H_{11}O_5N$ requires N, 5·7 per cent.)

Clemmensen Reduction of 4-phenyl-acetyl-resorcinol-preparation of 4-(B-phenyl-ethyl)-resorcinol).—A mixture of 4-phenyl-acetyl-resorcinol (2 gm.), amalgamated zinc (7 gm.) and hydrochloric acid (1:1; 60 c.c.) was heated on sand-bath under reflux for eight hours. The mixture on cooling was extracted with ether and the latter was shaken thrice with 5 per cent. solution of caustic soda. On acidifying the alkaline solution, a brown precipitate was obtained which crystallised from alcohol in pale-yellow needles m.p. 133–134° C.

Its alcoholic solution gave no coloration with ferric chloride. It was soluble in usual organic solvents. (Found : C, 78·3 H, 6·4; $C_{14}H_{14}O_2$ requires C, 78·5 × H, 6·5 per cent.)

Kostanecki Reaction of 4-phenyl-acetyl-resorcinol-Preparation of 7-hydroxy-2-methoxy-3-phenyl chromone and 7-acetoxy-2-methyl 3-phenyl chromone.—A mixture of 4-phenyl-acetyl-resorcinol (3 gm.) anhydrous sodium acetate (3 gm.) and acetic anhydride (25 c.c.) was heated in an oil-bath at 180–190° C. for 16 hours. It was then poured in water and the solid was treated with 5% alkali. The alkali soluble product crystallised from alcohol in pale-yellow, lustrous needles m.p. 244–246° C. It was soluble in alcohol, benzene, acetic acid and acetone, and dissolved in concentrated sulphuric acid giving bluish-purple flouores cence. (Found: C, 75·9; H, 4·68; $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·82 per cent.)

The alkali insoluble product, crystallising from alcohol in shining needles m.p. 165–166° C. was *7-acetoxy-2-methyl-3-phenyl chromone.*—It dissolved in concentrated sulphuric acid giving bluish-purple fluorescence. (Found: C, 73·3; H, 4·6; $C_{18}H_{14}O_4$ requires C, 73·5; H, 4·8 per cent.)

Conversion of 7-acetoxy-2-methyl-3-phenyl chromone into 7-hydroxy-2-methyl-3-phenyl chromone.—A solution of 7 acetoxy-2-methyl-3-phenyl-chromone (0·2 gm.) in concentrated sulphuric acid (5 c.c.) was allowed to stand overnight and poured over ice. The solid crystallised from alcohol in pale-yellow needles m.p. 244–246° C. undepressed by the pure sample of 7-hydroxy-2-methyl-3-phenyl-chromone.

Hydrolysis of the chromone by 5 per cent. alkali.—The above chromone (0·2 gm.) was refluxed with 5 per cent. sodium hydroxide (15 c.c.) on water-bath for three hours. The solution on acidification with hydrochloric acid gave a solid which crystallised from alcohol in long, yellow needles m.p. 115–116° C. undepressed by 4-phenyl acetyl-resorcinol.

Bromination of 7-hydroxy-2 methyl-3-phenyl-chromone with one mol. of bromine and Preparation of diperbromide of 7-hydroxy-2-methyl-3-phenyl chromone.—A solution of bromine (0·2 c.c.) in chloroform (10 c.c.) was gradually added to a cold solution of 7-hydroxy-2- methyl-3-phenyl chrome (1 gm.) in chloroform (30 c.c.) with constant shaking and kept overnight. The substance crystallised from chloroform in yellow needles m.p. 282–283°C. (Found: Br. 38·9; $C_{16}H_{12}O_3$. Br_2. requires Br. 38·8 per cent.)

Action of sulphur dioxide water on the di-perbromide of 7-hydroxy-2-methyl-3-phenyl-chromone.—The above perbromide (0·2 gm.) was allowed to stand for 24 hours with an aqueous solution of sulphur dioxide (50 c.c.), filtered, and crystallised from chloroform in white needles m.p. 244–246° C. undepressed by 7-hydroxy-2-methyl 3-phenyl-chromone.

Action of glacial acetic acid on di-perbromide of 7-hydroxy-2-methyl-3-phenyl-chromone.—The dibromide (0·2 gm.) was heated with glacial acetic acid (10 c.c.) on water-bath under reflux for three hours. The solution was then poured in large quantity of water and the solid was crystallised from chloroform in white needles m.p. 282–283° C. undepressed by the original di-perbromide.

B. Synthesis and properties of 4-phenylacetyl-pyrogallol 4-phenylacetyl pyrogallol.—prepared either by Nencki method (yield = 60 per cent.) or Friedel-crafts Method (yield = 50 per cent.) crystallised from alcohol in brown needles m.p. 144–145° C. Its alcoholic solution gave deep violet coloration with ferric chloride. (Found: C, 68·6; 4·8. $C_{14}H_{14}O_4$ requires C, 68·8; H, 4·9 per cent.)

The 4-*nitrophenyl hydrazone* crystallised from alcohol in short, reddish needles m.p. 223–224° C. (Found: N, 10·8. $C_{20}H_{17}O_5N_3$ requires N, 11·1 per cent.)

The 2:4-*dinitrophenylhydrazone* crystallised from alcohol in orange needles m.p. 242-244°. (Found: N, 12·4; $C_{20}H_{16}O_7N_4$ requires N 12·2 per cent.)

The Triacetyl derivative crystallised from dilute acetic acid in short needles m.p. 140° (depressed by the original ketone to 120°). Its alcoholic solution did not give any coloration with ferric chloride. (Found: C, 64·6; H, 4·7. $C_{20}H_{18}O_7$ requires C, 64·8; H, 4·8 per cent.)

The Tribenzoyl derivative crystallised from alcohol in needles m.p. 153–154°. (Found: C, 75·3; H, 4·1. $C_{35}H_{24}O_7$ requires C, 75·6; H, 4·3 per cent.)

6-*Bromo*-4-*phenylacetylpyrogallol* crystallised from alcohol in pale-yellow needles m.p. 155–156° C. (Found: Br., 24·5. $C_{14}H_{11}O_4$ Br. requires Br., 24·8 per cent.)

6-*nitro*-4-*phenylacetyl pyrogallol* crystallised from benzene in small, brown needles m.p. 179–180°. (Found: N, 4·6. $C_{14}H_{11}O_6$ N requires N, 4·8 per cent.)

4-(*B-phenyl-ethyl*)-*pyrogallol* crystallised from alcohol in pale-yellow plates m.p. 137–138° (depressed to 105 by the original ketone). (Found: C, 72·7; H, 5·9. $C_{14}H_{14}O_3$ requires C, 73·0; H, 6·1 per cent.)

7:8-*dihydroxy*-2-*methyl*-3-*phenyl-chromone* crystallised from alcohol in yellow needles m.p. 221-222°. It dissolved in concentrated sulphuric acid with red colour, and gave the original ketone on alkaline hydrolysis. (Found: C, 71·5; H, 4·3. $C_{16}H_{12}O_4$ requires C, 71·7; H, 4·5 per cent.)

The Di-perbromide crystallised from chloroform in yellow needles m.p. 287–288°. It gave the original chromone on treatment with aqueous sulphurous acid, while its solution in glacial acetic acid remained unchanged on heating. (Found: Br., 37·2; $C_{16}H_{12}O_2$ Br_2 requires Br., 37·4 per cent.)

We are thankful to Rev. Father A. M. Coyne S. J. for the provision of facilities.

Summary

The preparation and properties of 4-phenylacetyl-resorcinol and 4-phenyl-acetyl-pyrogallol have been described.

Reference

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THE FRIES REACTION

Part I. The Rearrangement of the Esters of Hydroxy-Coumarins

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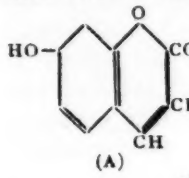
THE Fries Reaction which is one of the convenient methods for the synthesis of hydroxyketones has been studied exhaustively with the esters of monohydric phenols, though much systematic work has not been done with those of polyhydric phenols. Among the esters of the hydroxy derivatives of heterocyclic compounds, some work has been done with the esters of hydroxy-Coumarins by various workers,[1] but not with a view to determining the effect of (*a*) temperature, (*b*) quantity of the aluminium chloride, (*c*) nature of the acyl group, (*d*) and the nature of the phenolic compound. Though our study has been mainly concerned with the last factor, *i.e.*, the effect exerted by the nature and position of the substituents present in the phenolic portion on the Fries migration, we have found that the most suitable temperature for the change is 150–160° C.; and the time period varying from one to one and a half hour. From our experience of the Fries migration of the esters of polyhydric phenols, we find that three mols. of aluminium chloride are required for one mol. of hydroxy-coumarins, while one mol. of dihydroxy coumarins requires four mols. of aluminium chloride. Nitrobenzene as a solvent is advanta geous if the migration is to be studied at the ordinary temperature as a homogeneous solution is obtained. Less amounts of aluminium chloride leads to either deacetylation alone or partial migration. The acetyl group migrates more readily than the benzoyl group, but no comparative data has been studied.

7-acetoxy-coumarins were shown by Limaye (*loc. cit.*) to furnish 8 acetyl-7-hydroxy coumarins (main product) together with small quantities of 6-acetyl-isomers. If 8-acetyl-7-acetoxy-coumarins are taken, no Fries migration occurs, and deacetylation takes place, with the formation of the original 8-acetyl-coumarin. However, 6-acetyl-7-acetoxy coumarins give 6: 8-diacetyl-7-hydroxy coumarins. The presence of alkyl groups in 6 or 8 positions do not interfere with this reaction. The diacetoxy derivatives of 7: 8-dihydroxy coumarins and 6 : 7-dihydroxy coumarins undergo deacetylation only 6-acetoxy-4-methyl coumarin, 6-acetoxy-4 : 7-dimethyl coumarin and 6-acetoxy-4-phenyl coumarin underwent deacetylation, while 6-acetoxy-7-methyl coumarin gave 6-hydroxy-5-acetyl 7-methyl coumarin;

thus showing that the inability of 6-acetoxy-4-methyl coumarins to undergo the reaction was due to steric hindrance by the substituent in 4 position. 5:7-diacetoxy-4-methyl coumarin underwent the Fries Reaction giving a mixture of 6:8-diacetyl-and 6 or 8-acetyl-5:7-dihydroxy-4-methyl coumarin. The acelates of 7-hydroxy-3:4-dialkyl, and 5-hydroxy-3:4-dialkyl-coumarins gave identical migration products as their parent compounds.

Limaye (*loc. cit.*) observed that 7-acetoxy-2-methyl-3-acetyl chromone underwent deacetylation. We found that 5-acetoxy-3-acetyl-2-methyl, and 6-acetoxy-3-acetyl-2-methyl chromones did not undergo this reaction, and only deacetylation took place. The above results could be explained on basis of the coumarin structure postulated by Rangaswamy and Sheshadri[2] as a result of the theory of the Fixation of Double-Bonds put forward by Mills and Nixon,[3] and the migration of the acyl group along the double bond from oxygen to the second carbon. Of the three possible forms (A, B and C), A is the most stable, but the possibility of B or C is not ruled out to explain the migration of the acyl group of 7-acetoxy-coumarins to position 6. To explain the non-migration of acyl groups in the case of 7:8-diacetoxy and 6:7-diacetoxy coumarins, the formation of ring compounds containing aluminium (D and E) are assumed. On these assumptions we could predict the positions which acyl groups would occupy when the acetoxy derivatives of the following unknown coumarins would be subjected to this reaction. 8-Acetoxy-coumarins would give 7-acyl-8-hydroxy-coumarins, while 5:6-diacetoxy coumarins would undergo deacetylation 5:8-diacetoxy-coumarins would give either 6-acyl-5:8-dihydroxy or 7-acyl-5 : 8-dihydroxy coumarins, while 6 : 8-diacetoxy-coumarins would yield 7-acyl-6:8-dihydroxy-coumarins, if the position 4 is also substituted. In case position 4 is unsubstituted they would furnish 5:7-diacyl-6:8-dihydroxy coumarins. Experiments to synthesise some of these unknown coumarins to test these views are in progress.



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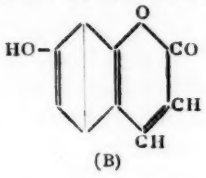

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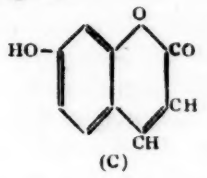

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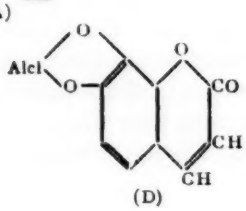

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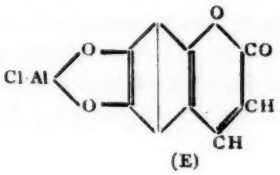

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Experimental

The Fries migration of 7-acetoxy-8-ethyl-4: 5-dimethyl coumarin and formation of 7-hydroxy-6-acetyl-8-ethyl-4: 5-dimethyl-coumarin.—An intimate mixture of the coumarin (1 g.) and aluminium chloride (1·5 g.) was heated at 150-160 for 1½ hours. After decomposing the mixture with ice-cold water the solid crystallised from alcohol in needles m.p. 124° (yield = 0·5 g.). Its alcoholic solution gave red coloration with ferric chloride. (Found: C, 69·0; H, 6·4. $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·2 per cent.)

Condensation of 2-methylhydroquinone with malic acid and formation of 7-methyl-6-hydroxy-coumarin. The solution of the phenol (3 g.), and malic acid (5 g.) in 85 per cent. sulphuric acid (50 c.c.) was heated on water-bath for three hours, and was poured on ice. The solid crystallised from alcohol in colourless, lustrous needles m.p. 210° (yield = 45 per cent.). It dissolves in alkali with a pale yellow colour giving no fluorescence. (Found: C, 68·1; H, 4·6. $C_{10}H_8O_3$ requires C, 68·2; H, 4·5 per cent.)

The acetyl derivative crystallised from alcohol in colourless needles m.p. 151° C. (Found: C, 65·7; H, 4·7. $C_{12}H_{10}O_4$ requires C, 66·0; H, 4·6 per cent.)

Fries migration of 6-acetoxy-7-methyl coumarin, and Formation of 6-hydroxy-5-acetyl-7-methyl coumarin.—An intimate mixture of the above acetoxy coumarin (1 g.) and aluminium chloride (1·5 g.) was heated at 150°–160° for two hours. The product on crystallisation from benzene gave the first crop of 6-hydroxy-coumarin, while the mother-liquor on evaporation gave a solid which crystallised from alcohol in needles m.p. 152° (depressed by the original compound to 130–135°). Its alcoholic solution gave red coloration with ferric chloride (yield = 0·3 g.). (Found: C, 66·2; H, 4·7. $C_{12}H_{10}O_4$ requires C, 66·0; H, 4·6 per cent.)

The p-*nitrophenylhydrazone* of the above compound crystallised from alcohol in orange needles m.p. 272°. (Found: N, 12·0; $C_{18}H_{15}O_{15}N_3$ requires N, 11·9 per cent.)

Fries migration of 5:7-diacetoxy-4-methyl coumarin, and Formation of 6-or 8-acetyl-5: 7-dihydroxy coumarin and 6: 8-diacetyl-5: 7-dihydroxy-coumarin.—The Reaction was carried out as usual. The product (0·85 g.) on crystallising from alcohol gave two equal fractions: (1) Needles m.p. 298° which was identified as 6 or 8-acetyl derivative by direct comparison with an authentic specimen of Shah and Shah (*loc. cit.*); (2) Needles m.p. 164°, the alcoholic solution of which gave blackish red coloration with ferric chloride. It was found to be the 6: 8-diacetyl derivative. (Found: C, 60·6; H, 4·5. $C_{14}H_{12}O_6$ requires C, 60·9; H, 4·3 per cent.)

Condensation of 1:2:4-*triacetoxy benzene with Ethy aceto-acelate and formation of* 6:7-*dihydroxy coumarin.*—This triacetoxy benzene was prepared by the action of acetic anhydride on *p*-benzoquinone according to the method of Thiele.[4] The solution of triacetoxy benzene (5 g.), and ethyl aceto-acetate (5 g.) in 73 per cent. sulphuric acid (25 c.c.) was kept overnight, and poured into water. The solid crystallised from alcohol in needles m.p. 269–270° which was 6: 7-dihydroxy-4-methyl coumarin.

The dimethyl ether obtained by methylating with dimethyl sulphate crystallised from dilute alcohol in needles m.p. 144°.

Hydrolysis of 6: 7-*dihydroxy-coumarin in presence of dimethyl sulphate and Formation of cis* 3: 4: 6-*tri-methoxy-B-methylcinnamic acid.*—To the solution of the coumarin (1 g.) in acetone (20 c.c.), dimethyl sulphate (10 c.c.) and sodium hydroxide (25 c.c. of 20 per cent. solution) was added, and the mixture refluxed on the water-bath, for one hour and a half. Further quantities of dimethyl sulphate (5 c.c.) and alkali (10 c.c.) were added. The cooled solution, on acidification with hydrochloric acid gave an acid which crystallised from dilute alcohol in lemon yellow, prismatic needles m.p. 150–151°. As the acid was unaffected by heat or light, and underwent cyclisation with concentrated sulphuric acid giving 6: 7-dimethoxy-4-methyl coumarin, it had the cis-configuration. (Found: C, 61·7; H, 6·4. $C_{13}H_{16}O_5$ requires C, 61·9; H, 6·3 per cent.

The diacetoxy-derivative of the coumarin) m.p. 134° (1g.) was converted into the original dihydroxy coumarin on heating with aluminium chloride (2 g.) at 150–160° for two hours.

We take this opprtunity of thanking the Rev. Father A. M. Coyne, S.J., for his kind interest in this work.

Summary

The Fries Reaction of some 7-acetoxy,-6-acetoxy,-7: 8-diacetoxy and 6: 7-diacetoxy coumarins has been studied, and explanation has been given for the failure as well as the success of the reaction.

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A NOTE ON THE NUCLEAR METHYLATION OF LECANORIC ACID

By V. Venkateswarlu

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Received February 5, 1947

(Communicated by Prof. T. R. Seshadri)

In the course of work on lichen acids a synthetic sample of rhizonic acid was required. The simplest method of synthesis is that of Robinson and Shah[1] using the nuclear methylation of ethyl orsellinate and subsequent hydrolysis. But orsellinic acid itself is difficult to obtain synthetically. Though this acid does not occur in lichens free, the ethyl ester can be easily made from lecanoric acid and then subjected to nuclear methylation. In order to simplify the preparation, lecanoric acid obtained from Parmelia abessinica[2] has been directly treated with excess of methyl alcoholic potash and methyl iodide. The didepside undergoes simultaneous nuclear methylation and alcoholysis yielding methyl rhizonate.

Experimental

To a solution of caustic potash (5·6 g., 10 mols.) in anhydrous methyl alcohol (60 c.c.) lecanoric acid (3·2 g.) was added. The solid dissolved to give a clear red solution. On cooling in a freezing mixture, the solution set to a thick cake. Enough methyl alcohol was added to allow stirring and shaking at the temperature of the freezing bath and then the mixture was treated with excess of ice-cold methyl iodide (30 c.c., 12 mol.) all at once. The contents of the flask was shaken to form a uniform mixture and the flask left stoppered in the ice-bath and allowed to assume laboratory temperature overnight. The dark red clear solution had deposited some crystals of potassium iodide by next morning. The mixture was gently boiled under reflux for eight hours after the addition of some more methyl iodide (5 c.c.) to make up for losses. It was then treated with ice-water (300 c.c.) and left overnight. As much of the alcohol as possible was then removed by distillation under reduced pressure and the highly coloured solid product was filtered and dried in a vacuum desiccator. The solid (2 g.) was then purified in the following manner. It was dissolved in the minimum quantity of dry acetone and petroleum ether was added until coloured impurities separated out leaving the solution clear and almost colourless. It was then decanted and concentrated when a pale yellow liquid with a small amount

of the coloured impurities separated out. Repetition of the above process removed the rest of the colour. Methyl rhizonate was finally purified by crystallisation from ethyl alcohol when it came out as shining clusters of colourless needles melting at 95–96°. (Found: C, 63·0; H, 7·0; $C_{11}H_{14}O_4$ requires C, 62·9; H, 6·7%.)

The above ester was hydrolysed using aqueous alkali (20%) and keeping the solution at the laboratory temperature for 24 hours. The clear solution was then acidified and the precipitated acid crystallised from dilute alcohol when it came out as colourless needles melting at 235°. This acid was found to be identical with a sample of rhizonic acid obtained by the nuclear methylation of ethyl orsellinate.

The author expresses thanks to Prof. T. R. Seshadri for his interest in this work.

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INSECTICIDAL PROPERTIES AND CHEMICAL CONSTITUTION

Part II. Coumarins

By V. V. Sreerama Murti and T. R. Seshadri

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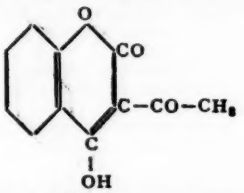
In Part I[1] it was shown that the methyl ethers of some of the simpler flavones are markedly toxic to fish. They have in them the characteristic toxophore $-CO-C=C-O-$ also found in rotenone. Results recorded by previous workers relating to the simpler coumarins having the toxophore $-C=C-CO-O-$ suggest that they are comparatively feeble. Späth[2] found that 175·5 mg. of 4-methyl umbelliferone and 63·7 mg. of 7-ethoxy coumarin per litre of water were necessary for causing death of fish in 8 hours. The more potent among the compounds studied by him contain also furan rings and other complications. Later Mahal[3] noted that 4-methyl umbelliferone does not possess appreciable anthelmintic properties. Again Läuger *et al.*[4], though they have not presented details, have reported that the simpler coumarins have only weak insecticidal properties. They observed very good strength only in the case of 4-hydroxy coumarins with a carbonyl substituent in the 3-position (I). This discovery was based on the similarity in structure between those compounds and dehydracetic acid (II) which has also very good insecticidal properties.



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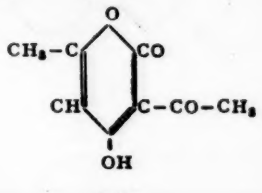
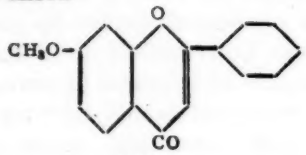


(II)

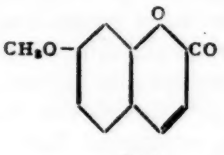
It appeared to be necessary to study the cause of this marked difference in toxicity between the simple coumarins and the simple flavones. An examination of a number of simple coumarin derivatives employing fish and the 'turning time' as a measure of toxicity has now established that they have weak toxic properties. For example, 7-hydroxy flavone takes

about 12 hours to show toxic symptoms in a concentration of 20 mg. per litre whereas for umbelliferone a concentration of more than 200 mg. per litre is found to be necessary; 7-methoxy flavone (III) in a concentration of 10 mg. per litre has a 'turning time' of 5·5 minutes while 7-methoxy coumarin (IV) is required in a concentration of 100 mg. per litre to produce the toxic effect in about 7 minutes.

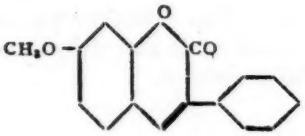
It appeared to be possible that the above difference may not all be due to the difference in the toxophores, but due to the absence of a side phenyl nucleus in the coumarins studied. Consequently, 3-phenyl and 4-phenyl umbelliferones and their methyl ethers (V and VI) were tested. These compounds are considerably more toxic and compare favourably with the isomeric flavone derivatives. 3-Phenyl umbelliferone seems to be even better than 7-hydroxy flavone. The methyl ethers are somewhat weaker than 7-methoxy flavone; however, they seem to have the same order of toxicity. Isomerism in the methyl ethers of the phenyl coumarins does not seem to make much difference in toxicity though in the case of the hydroxy compounds difference in the position of the side phenyl nucleus seems to have a marked effect.



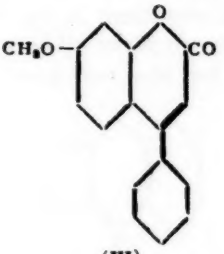
(III)



(IV)



(V)



(VI)

The data obtained in the experiments carried out with a large number of coumarin derivatives are given in the accompanying table. One important point that emerges from these results relates to the marked effect of concentration in many of the compounds of the weak type. Below what might be considered as the critical concentration, the effect seems to drop off very markedly; on the other hand above that concentrations the rise in toxicity is also marked.

(ge.)=gelatin added

Name of the Compound	Concentration, milligrams per litre	Turning time
1. 7-Methoxy flavone ..	10	5·5 min.
2. Umbelliferone ..	200	12 hrs.
	100	No effect in 24 hrs.
3. 7-Methoxy coumarin ..	150	3·0 min.
	100	6·5 ,,
	20 and 50	No effect in 5 hrs.
4. 3-Phenyl umbelliferone ..	100 ge.	3·5 min.
	30 ,,	15·0 ,,
	20 ,,	29·0 ,,
5. 3-Phenyl-7-methoxy coumarin ..	10 ,,	9·0 ,,
	5 ,,	28·5 ,,
6. 4-Phenyl umbelliferone ..	100 ,,	5·0 ,,
	80 ,,	35·5 ,,
7. 4-Phenyl-7-methoxy coumarin ..	20 ,,	5·0 ,,
	10 ,,	11·5 ,,
	5 ,,	31·0 ,,
8. 7-Hydroxy-5-methyl-3-phenyl coumarin ..	40 ,,	10·0 ,,
	20 ,,	16·5 ,,
9. 7-Methoxy-5-methyl-3-phenyl coumarin ..	10 ,,	18·0 ,,
10. 3-Acetyl-umbelliferone ..	200 ,,	29·5 ,,
11. 3-Acetyl-7-methoxy coumarin ..	20 ,,	No effect in 3 hrs.
12. 3-Benzoyl-7-methoxy coumarin ..	20 ,,	do
13. 3-Carbethoxy-7-methoxy coumarin ..	50 ,,	13·0 min.
	30 ,,	25·0 ,,
	20 ,,	42·0 ,,
14. 4-Methyl umbelliferone ..	200	34·5 ,,
	150	58·0 ,,
	100	No effect in 20 hrs.
15. 4-Methyl-7-methoxy coumarin ..	100 ge.	6·0 min.
	67 ,,	11·0 ,,
	50 ,,	25·5 ,,
	33 ,,	About 15 hours
16. 5-Methoxy-4 methyl coumarin ..	30	3·0 min.
	20	5·0 ,,
	10	No effect in 18 hrs.
17. 5-Hydroxy-4:7-dimethyl coumarin ..	200 ge.	39·5 min.
18. 5-Methoxy-4:7-dimethyl coumarin ..	40 ,,	7·0 ,,
	20 ,,	12·5 ,,
19. 6-Hydroxy-4-methyl coumarin ..	200	11·5 ,,
20. 6-Methoxy-4-methyl coumarin ..	100 g.	25·0 ,,
21. 7-Hydroxy-5-methyl coumarin ..	200 ,,	27·0 ,,
	100 ,,	No effect in 24 hrs.
22. 5:7-Dihydroxy-4-methyl coumarin ..	200 ,,	do
23. 5:7-Dimethoxy-4-methyl coumarin ..	20 ,,	14·5 min.
	10	34·0 ,,
24. 7:8-Dihydroxy-4-methyl coumarin ..	200	No effect in 12 hrs.
25. 7:8-Dimethoxy-4-methyl coumarin ..	50 ge.	19·0 min.
	30 ,,	No effect in 4 hrs.
26. 5:7-Dihydroxy-3-phenyl coumarin ..	30 ,,	No effect in 16 hrs.
27. 5:7-Dimethoxy-3-phenyl coumarin ..	10 ,,	No effect in 5 hrs.

In the case of a number of compounds in which the solubility in water is inadequate for the purpose of the experiments, it has been found that the concentration could be considerably increased by the preliminary addition of gelatin; ordinarily about one gram per litre of water is found

to be adequate. That gelatin has no effect on the toxic properties under these conditions has been proved by means of blank and comparative experiments.

Amongst the number of the coumarin derivatives examined the 5-methoxy compounds appear to show some promise though they are more difficult to prepare. A more detailed study of this type of compounds will be described later. A methyl group situated in the 4-position seems to have a favourable influence. But a further addition of this group in the 7-position decreases the effect. An interesting point relates to the comparative effect of an acetyl, carbethoxyl, and phenyl groups in the 3-position of the umbelliferones and their methyl ethers. The results suggest that as given above they are in the rising order of toxicity, whereas Lauger *et al.* using compounds devoid of the hydroxyl and methoxyl groups found that 3-acetyl (as in 3-acetyl coumarin) is somewhat more powerful than the phenyl or carbethoxyl.

Summary

The simpler coumarins are considerably less toxic as compared with the simpler flavones. This could be attributed to the lack of a side-phenyl nucleus in the former. 3-Phenyl and 4-phenyl umbelliferones and their methyl ethers are found to be highly toxic and compare favourably with 7-hydroxy and 7-methoxy-flavones. A large number of related coumarin derivatives have been studied for their toxicity towards fish.

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INSECTICIDAL PROPERTIES AND CHEMICAL CONSTITUTION

Part III. Some Partial Methyl Ethers of Hydroxyflavones

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Received February 5, 1947

A NUMBER of partial methyl ethers of flavones and flavonols occur in plant drugs. In several cases they seem to be the only special components present. Examples are calycopterin from the leaves of *Calycopteris floribunda*, gardenin from the gum of *Gardenia lucida*, tambulin from the seeds of *Zanthoxylum acanthopodium* and oroxylin-A from the root bark of *Oroxylum indicum*. Very little is known about the physiological properties of these compounds. Among these plant drugs the copper coloured tender leaves of Calycopteris floribunda have been reputed to have anthelmintic properties.[1] In their account of the isolation of calycopterin from this source, Ratnagiriswaran, Sehra and Venkataraman[2] stated that this compound had been found to be toxic to round worms and clinical trials conducted in the General Hospital, Madras, had given encouraging results. Later Mahal[3] could not confirm these findings using as experimental animals round worms, tape worms and leeches. In view of the interesting results reported in Part I[4] of this series of papers that ethers of simple hydroxy flavones exhibit definite toxicity to fish, the toxic properties of calycopterin and its methyl ethers have now been investigated using these animals.

From the experimental data given later it will be clear that calycopterin and its mono and dimethyl ethers are definitely toxic to fish. Calycopterin dimethyl ether is markedly more toxic than the isomeric hexamethyl ethers of myricetin and quercetagetin. It has already been pointed out that the presence of more than one methoxyl in the side phenyl nucleus diminishes toxicity markedly. But calycopterin dimethyl ether (calycopteretin-hexamethyl ether) is even more toxic than the pentamethyl ether of herbacetin which like it has also only one methoxyl group in the side-phenyl nucleus. Hence it appears that the presence of one more methoxyl in the benzopyrone part enhances toxic properties. Calycopterin itself is less toxic than its dimethyl ether as could be normally expected.

The most interesting data are provided by the two isomeric monomethyl ethers of calycopterin. The 4'-monomethyl ether having a free

hydroxyl in the 5-position is markedly more toxic than even the dimethyl ether and the 5-mono-methyl ether on the other hand is only feebly toxic. Thus a free hydroxyl in the 5-position seems to be desirable for enhanced toxicity and a free hydroxyl in the side-phenyl nucleus (4′-position) appears to be unfavourable. These points seem to be supported by some of our past experiments. For example, galangin (3:5:7-trihydroxy flavone) was found to be much more toxic than 3:7-dihydroxy flavone and kæmpferol (3:5:7:4′-tetrahydroxy flavone) had only feeble toxicity. Again chrysin, as shown in this paper, is considerably more toxic than 7-hydroxy flavone. The moderate toxicity of calycopterin is obviously the resultant effect of the two hydroxyls in the 5 and 4′-positions superimposed on the completely oxidised benzopyrone structure and this may be an advantage in an anthelmintic which has to be administered internally. Further this structure appears to confer on the compound a desirable degree of water and lipoid solubility.

Among the number of partial methyl ethers that were examined in the course of this work there are some simpler compounds that have a free hydroxyl group in the 5-position. They do not exhibit the toxic properties so markedly shown by calycopterin and its 4′-methyl ether. It should therefore be concluded that the correlation between structure and toxic properties is complex and cannot be analysed in a simple manner. A comparison of 7-hydroxy flavone with 3:7-dihydroxy flavone and 3-methoxy-7-hydroxy-flavone and of chrysin with galangin and its 3-methyl ether would indicate that the addition of a hydroxyl in the 3-position of these simple structures is favourable to toxicity and that its methylation is a disadvantage.

In our attempts to prepare calycopterin we had occasion to examine the mature green leaves of *C. floribunda* obtained from the Cuddappah district of the Deccan plateau. The ether and acetone extracts of these leaves were definitely toxic to fish and they were found to contain calycopterin. Extraction using the method of Shah *et al.*[7] revealed that these form a better source of calycopterin (0·4% of the air dry leaves) than the copper coloured tender leaves and consequently these mature leaves could be used with advantage; further they are more easily available.

A convenient method of preparing the dimethyl ether from calycopterin using dimethyl sulphate in dry acetone medium has recently been described.[5] The synthetic sample of this substance made by the method of total synthesis[6] has also been used for the test and found to give the same result. The 4′-monomethyl ether was originally prepared by Shah,

Virkar and Venkataraman[7] by partial methylation using diazomethane. It has now been obtained more easily using dimethyl sulphate and purified by working through its potassium salt. The 5-monomethyl ether is a synthetic sample prepared by the method of Seshadri and Venkateswarlu.[8]

Experimental

Preparation of 4'-O-*methyl calycopterin*: (3:6:7:8:4'-*pentamethoxy-5-hydroxy flavone.*—A solution of pure calycopterin (1·0 g.) in a mixture of acetone (25 c.c.) and benzene (50 c.c.) was treated with dimethyl sulphate (0·27 c.c.: 1·1 mol.) and anhydrous potassium carbonate (5 g.). After refluxing for 6 hours the solvents were removed and the residue treated with water (20 c.c.). The precipitated yellow solid was filtered and washed. It was dissolved in the minimum of absolute alcohol, treated with absolute alcoholic potash (0·5 g. in 5 c.c. of absolute alcohol) and the deep red solution was evaporated to dryness quickly on a water-bath. The orange yellow solid was washed repeatedly with hot benzene to remove any dimethyl ether that might be present. The residue was treated with water acidified with hydrochloric acid, heated for a minute in a boiling water-bath and filtered. The yellow solid was crystallised from alcohol from which it

(*ge.*) = *gelatin added*

Name of the substance	Concentration in milligrams per litre	Turning time
1. Calycopterin ..	30	15·0 min.
	20	30·0 ,,
	10	73·0 ,,
2. Calycopterin dimethyl ether ..	30	11·5 ,,
	20	21·0 ,,
	10	54·0 ,,
3. Calycopterin-5-monomethyl ether ..	30 }	More than 4 hours
	20 }	
	50	63·0 min.
4. Calycopterin-4'-monomethyl ether ..	5	42·0 ,,
	7	25·0 ,,
	8	14·5 ,,
	10	11·5 ,,
5. 7-Hydroxy-3-methoxy flavone ..	20	About 3 hours
	50	25·5 min.
6. Chrysin ..	20 (*ge.*)	27·5 ,,
7. Oroxylin-A ..	20 (*ge.*)	28·0 ,,
8. Gardenin methyl ether ..	20	71·0 ,,
	30	28·0 ,,
	50	12·0 ,,

separated in the form of golden yellow, stout, rhombohedral prisms melting at 126-27° (Shah *et al.*, m.p. 124°); yield, 0·6 g. It was sparingly soluble in aqueous sodium hydroxide even on heating and gave an olive green colour with alcoholic ferric chloride.

Similar procedure was adopted for preparing galangin-3:7-dimethyl ether, kæmpferol-3:7:4′-trimethyl ether and quercetin-3:7:3′:4′-tetramethyl ether.

Gardenin[9] (20 mg.), galangin-3-methyl ether (20 and 30 mg.), izalpinin[10] (10 and 20 mg.), galangin-3:7-dimethyl ether (10 mg.), kæmpferol-3:7:4′-trimethyl ether (30 mg.), quercetin-3:3′:4′-trimethyl ether (30 mg.), and quercetin 3:7:3′:4′-tetramethyl ether were not found to be appreciably toxic. The compounds that have only one hydroxyl group in the 5-position are very sparingly soluble in water; with higher concentrations, only colloidal and non-clear solutions were obtained with the help of gelatin (1 gram for one litre of water used).

Summary

A number of partial methyl ethers of hydroxy flavones and related compounds have been tested for toxicity to fish and the results are discussed with reference to structural characteristics. Calycopterin and its 4′-methyl ether are markedly toxic.

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HETEROCYCLIC COMPOUNDS

Part XVII. Coumarins from β-ketonic Esters and 5 methyl-2-ethyl, 5-methyl-2-propyl-, 5-methyl-2: 4-diethyl-4-Ethyl-2-benzoyl-resorcinols, and Phlorobenzophenone

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Received September 30, 1946

In continuation of the previous work of Desai and co-workers on the coumarins from substituted resorcinols, we have studied the coumarin condensation between some new resorcinols which we happened to synthesise and ethyl acetoacetate and its alkylated derivatives. Thus 5-methyl-2-ethyl-resorcinol and 5-methyl-2-propyl-resorcinol condensed readily with ethyl-acetoacetate giving 7-hydroxy-4: 5-dimethyl-8-ethylcoumarin, and 7-hydroxy-4: 5-dimethyl-8-propyl-coumarin in presence of concentrated sulphuric acid. The alkylated aceto-acetic esters behaved similarly. However, 5-methyl-2: 4-diethyl-resorcinol gave the expected 7-hydroxy-4: 5-dimethyl-6: 8-diethyl-coumarin with aceto-acetic ester only in the presence of anhydrous aluminium chloride.

4-ethyl-2-benzoil-resorcinol condensed with aceto-acetic ester (H_2SO_4) with the formation of 4-methyl-6-ethyl-7-hydroxy-8-benzoyl-coumarin, the constitution of which was proved by its rational synthesis by the Fries migration of 7-benzoyloxy-4-methyl-6-ethyl-coumarin which was prepared by the benxzoylation of 7-hydroxy-4-methyl-6-ethyl-coumarin.

Phlorbenzophenone condensed with aceto-acetic ester giving 5: 7-dihydroxy-4-methyl-6 or 8-benzoyl-coumarin.

Experimental

(*A*) *Coumarins from 5-methyl-2-ethyl resorcinol.*—5-methyl-2-ethyl-resorcinol was prepared by the method of Desai and Vakil.[1]

4: 5-*Dimethyl-7-hydroxy-8-ethyl-coumarin.*—The mixture of 5-methyl-2-ethyl resorcinol (3 gms.), ethyl aceto-acetate (2.5 g.) and 73% sulphuric acid (50 c.c.) was kept at room temperature for twenty-four hours. On pouring the mixture over ice, the solid that separated out crystallised from alcohol in colourless needles m.p. 235° (yield 70 per cent). It dissolved in

caustic soda solution giving greenish pink fluorescence. (Found: C, 71·5; H, 6·6; $C_{13}H_{14}O_3$ requires C, 71·6; H, 6·4%.)

Its acetyl derivative crystallised from alcohol in lustrous needles m.p. 121°. (Found: C, 69·1; H, 6·3; $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·2%.)

3:4:5-*Trimethyl-7-hydroxy-8-ethyl-coumarin.*—Prepared from 5-methyl-2-ethyl-resorcinol and ethyl methyl-aceto-acetate crystallised from alcohol in colourless silky needles m.p. 227° C. (Found: C, 72·3; H, 7·3; $C_{14}H_{16}O_3$ requires C, 72·4; H, 7·1%.)

3:8-*Diethyl*-4:5-*dimethyl-7-hydroxy-coumarin* crystallised from alcohol in needles m.p. 192° C. (Found: C, 73·0; H, 7·6; $C_{15}H_{18}O_3$ requires C, 73·1; H, 7·4%.)

3-*propyl*-4:5-*dimethyl-7-hydroxy-8-ethyl-coumarin* crystallised from alcohol in lustrous needles m.p. 172°. (Found: C, 73·6; H, 7·9; $C_{16}H_{20}O_3$ requires C, 72·8; H, 7·8%.)

(*B*) *Coumarins from 5-methyl-2-propyl resorcinol.*—The above phenol was prepared by the clemmensen reduction of γ-orcpropiophenone which was prepared by the Fries migration of orcinol dipropionate as follows:—

A mixture of orcinol dipropionate (8 g.) and powdered anhydrous aluminium chloride (16 g.) was heated in an oil-bath at 145–150° C. for one hour and a half, and the cooled mass was decomposed with ice-cold water. The solid crystallised from dilute acetic acid in long, colourless needles m.p. 85–86°, and its alcoholic solution gave dark-red coloration with ferric chloride (yield, 60 per cent.). (Found: C, 65·9; H, 7·0; $C_{13}H_{16}O_4$ requires C, 66·1; H, 6·8%.)

The above *dipropionyl orcinol* (5 g.) was dissolved in 85 per cent. sulphuric acid (25 c.c.) and the solution was poured over ice after four hours, when a solid crystallising from dilute acetic acid in long needles m.p. 135° C. was obtained. The alcoholic solution of γ-orcpropiophenone gave green coloration with ferric chloride (yield = 3·0 g.). (Found: C, 66·5; H, 6·9; $C_{10}H_{12}O_3$ requires C, 66·6; H, 66·6%.)

The clemmensen reduction of the above γ-ketone with amalgamated zinc in the usual manner gave 5-methyl-2-*propyl-resorcinol* which crystallised from petroleum ether (b.p. 60–80°) in colourless needles m.p. 105°.

4:5-*dimethyl-7-hydroxy-8-propyl-coumarin* obtained from 5-methyl-2-propyl resorcinol and ethyl aceto-acetate using 73% sulphuric acid crystallised from alcohol in colourless needles m.p. 202°, and dissolved in dilute caustic soda with a yellow colour and greenish pink fluorescence. (Found: C, 72·2; H, 7·2. $C_{14}H_{16}O_3$ requires C, 72·4; H, 7·1%.)

3:4:5-*trimethyl*-7-*hydroxy*-8-*propyl-coumarin prepared* from 5-methyl-2-propyl resorcinol and ethyl methylaceto-acetate crystallised from alcohol in soft, colourless needles m.p. 192°. (Found: C, 73·0; H, 7·2; $C_{15}H_{18}O_3$ requires C, 73·2; H, 7·3%.)

3-*Ethyl*-4:5-*dimethyl*-7-*hydroxy*-8-*propyl-coumarin* crystallised from alcohol in short needles m.p. 180° C. (Found: C, 73·5; H, 7·8; $C_{16}H_{20}O_3$ requires C, 73·8, H, 7·7%.)

3:8-*dipropyl*-4:5-*dimethyl*-7-*hydroxy-coumarin* crystallised from alcohol in needles m.p. 168°. (Found: C, 74·2; H, 8·2; $C_{17}H_{22}O_3$ requires C, 74·5; H, 8·0%.)

2:4-*Diethyl*-5-*methyl-resorcinol* was obtained by heating a mixture of 2:4-diacetyl-5-methyl resoncinol (2·5 g.), amalgamated Zinc (20 g.) and dilute hydrochloric acid (60 c.c.) for five hours under reflux. The solid that separated out on cooling crystallised from benzene in soft needles m.p. 122°. (Found: C, 73·2; H, 9·0; $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·9%.)

4:5-*dimethyl*-6:8-*diethyl*-7-*hydroxy-coumarin.*—The solution of 2:4-diethyl-5-methyl-resorcinol (3·5 g.) ethylaceto-acetate (2·6 g.) and anhydrous aluminium chloride (6·0 g.) in nitro-benzene (40 c.c.) was heated in an oil-bath at 125–130° C. for two hours. After decomposing the mixture with ice-cold hydrochloric acid and removing the nitro benzene in steam, the residue crystallised from alcohol in straw-yellow needles m.p. 180°. Its yellow, alkaline solution gave green fluorescence. (Found: C, 73·0; H, 7·6. $C_{15}H_{18}O_3$ requires C, 73·1; H, 7·4%.)

Preparation of 4-*Ethyl*-2 *Benzoyl resorcinol. Preparation of* 7-*Benzoyloxy*-6-*ethyl*-4-*methyl-coumarin.*—The benzoylation of 7-hydroxy-6-ethyl-4-methyl coumarin (Desai and Ekhlas[3]) by the Schotten-Baumann method gave 7-benzoyloxy-6-ethyl-4-methyl-coumarin, which crystallised from alcohol in lustrous needles m.p. 157°. (Found: C, 73·8; H, 5·3; $C_{19}H_{16}O_4$ requires C, 74·0; H, 4·2%.)

8-*Benzoyl*-7-*hydroxy*-6-*ethyl*-4-*methyl-coumarin.*—An intimate mixture of the above benzoyloxy-coumarin (3 gms.) and anhydrous aluminium chloride (3 gms.) was heated in an oil-bath at 150–160° for an hour and half, and the cooled mixture was decomposed with ice-cold hydrochloric acid. The resulting solid on treatment with warm benzene left a considerable amount of the solid which was 7-hydroxy-6-ethyl-4-methyl coumarin, while the benzene soluble substance was recrystallised from alcohol in needles m.p. 133°. Its alcoholic solution gave dark-violet coloration with ferric chlorides while its alkaline solution was yellow and devoid of fluorescence. (Found: C, 74·0; H, 5·3; $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%.)

The yield of 8-benzoyl-7- hydroxy-6-ethyl-4-methyl coumarin was 40 per cent.

Hydrolysis of 8-benzoyl-7-hydroxy-6-ethyl-4-methyl coumarin to 4-ethyl-2-benzoyl resorcinol.—A solution of the above coumarin (1 g.) in 10 per cent. sodium hydroxide (15 c.c.) was heated under reflux for 4 hours. The filtered solution was acidified with hydrochloric acid, and the resulting solid was treated with sodium bicarbonate solution to remove some soluble impurities. The residue crystallised from alcohol in straw-yellow needles m.p. 128° (yield, 40 per cent.). Its alcoholic solution gave greenish coloration with ferric chloride. (Found: C 74·1; H, 5·9; $C_{18}H_{14}O_3$ requires C, 74·4; H, 5·8%.)

When the solution of the above phenol (1·2 g.) and ethyl aceto-acetate (0·7 g.) in 73% sulphuric acid (25 c.c.) was left at the ordinary temperature for 36 hours, and worked up as usual, the product that was obtained (1 g.) was identified by m.p. and mixed m.p. as 8-benzoyl-7-hydroxy-6-ethyl-4-methyl-coumarin.

4-methyl-5 : 7-dihydroxy-6 or 8-benzoyl-coumarin.—A solution of phloro-benzophenone (2 g.) and ethylaceto-acetate (1 g.) in 85% sulphuric acid (25 c.c.) was kept at the ordinary temperature for 36 hours. The solid obtained by pouring the solution in ice-cold water crystallised from alcohol in lustrous needles m.p. 322°. Its alcoholic solution gave reddish coloration with ferric chloride, while its yellow, alkaline solution was non-fluorescent. (Found: C, 68·6; H, 4·2; $C_{17}H_{12}O_5$ requires C, 68·9; 4·0%.)

We take this opportunity of expressing our thanks to Rev. Father A.M. Coyne, S.J., for his kind interest in this work.

Summary

Coumarins were prepared from β-ketonic esters and some new resorcinol derivatives which were prepared in connection with some other work, and it was observed that they varied in their capacity for condensation.

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2. ——— and (Miss) Vakil .. *Ibid.*, 1940, **12**, 393.
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HETEROCYCLIC COMPOUNDS

Part XVIII. Condensation of Cyclic-β-Ketonic Esters with Methyl-β-Resorcylate and Resacetophenone in Presence of Anhydrous Aluminium Chloride

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7-Hydroxy-coumarins from various open-chain as well as cyclic β-ketonic esters and resacetophenone have been prepared by Desai and co-workers[1] using phosphorous oxychloride as the condensing agent, while 5-hydroxy coumarins have been prepared by Shah and co-workers[2] from open-chain β-ketonic esters and methyl β-resorcylate as well as resacetophenone using anhydrous aluminium chloride as the condensing agent. As the condensation of cyclic β-ketonic esters with methyl β-resorcylate has not been studied, we have studied this reaction in presence of various condensing agents. We have also studied the coumarin condensation between the cyclic β-ketonic esters and resacetophenone in presence of anhydrous aluminium chloride.

Methyl β-resorcylate condensed with ethyl cyclohexanone-2-carboxylate in presence of sulphuric acid, phosphorous oxychloride or aluminium chloride giving only one product which was found to be 7-hydroxy-6-carbomethoxy-3:4-cyclohexeno-coumarin. This result was quite surprising, as Shah and co-workers (*loc. cit.*) had invariably obtained the 5-hydroxy-coumarins from open-chain β-ketonic esters and methyl β-resorcylate in presence of anhydrous aluminium chloride.

Resacetophenone, on the other hand, condensed with ethyl cyclohexanone-2-carboxylate in the presence of anhydrous aluminium chloride giving 5-hydroxy-6-acetyl-3:4-cyclohexeno-coumarin, thus simulating the behaviour of open-chain β-ketonic esters.

Identical results were obtained from ethyl cyclopentanone-2-carboxylate and ethyl 4-methylcyclopentanone-2-carboxylate. 7-Hydroxy-6-acetyl-3:4-cyclohexeno-and cyclopenteno-coumarin have been already described by Chowdhry and Desai (*loc. cit.*) while 5-hydroxy-6-acetyl-3: 4-cyclo hexeno- and -cyclopenteno-coumarins are described in the body of this paper. In order to complete our observation and compare their properties, the

isomeric 7-hydroxy-8-acetyl-3:4-cyclohexeno- and cyclopenteno-coumarins have been synthesised by the Fries migration of 7-acetoxy-3:4-cyclohexeno- and cyclopenteno-coumarins.

Shah and co-workers (*loc. cit.*) have suggested the stabilisation of one of the kekule forms of the benzene ring in resacetophenone and methyl β-resorcylate in virtue of the chelation between hydroxyl and acetyl as well as carbo-methoxy groups in order to explain the formation of 5-hydroxy coumarins. That the chelation does take place is amply borne out, not only by the work of Shah and co-workers[3] on coumarin condensations, and formylation of resorcinol derivatives, but also by the work of W. Baker and his co-workers[4] on distribution in resorcinol nucleus. The discrepancy noticed in this work regarding the inability of methyl β-resorcylate to give 5-hydroxy coumarins in presence of aluminium chloride leads us to the conclusion that the stabilisation of one of the kekule forms of the benzene ring due to chelation is of a transient or labile nature, in the case of this ester.

Experimental

(*A*) *Coumarins from ethyl cyclohexanone-2-carboxylate-7-hydroxy-6-carbomethoxy-3 : 4-cyclohexeno-coumarin.*—

(1) A solution of methyl β-resorcylate (2 g.) and the keto-ester (2 g.) in 73 per cent. sulphuric acid was kept in the refrigerator for two days, and poured into ice-cold water. The resulting solid was treated with dilute sodium bicarbonate solution to remove the acidic impurities, and the insoluble residue was crystallised from alcohol when colourless needles, m.p. 226°, were obtained (yield, 2·0 gm.).

(2) A mixture of the phenol ester (2 g.), keto-ester (2 g.) and phosphorous oxychloride (3·5 g.) was warmed on the water-bath for two hours. The residue was thrice extracted with benzene (25 c.c.) to remove the coumarin, and the solvent was removed from the combined extracts. The residue crystallised from alcohol in colourless needles, m.p. 226° (yield, 2·5 g.).

(3) A solution of the phenol ester (2 g.), keto-ester (2 g.) and anhydrous aluminium chloride (3·5 g.) in nitro-benzene (20 c.c.) was heated in oil-bath at 110–15° for two hours, and worked up as usual. The solid crystallised from alcohol in needles, m.p. 226°, undepressed by the sample prepared by methods (1) and (2) (yield, 2·5 gm.). Its alcoholic solution gave reddish violet coloration with ferric chloride, while its alkaline solution gave an intense blue fluorescence. (Found: C, 65·4; H, 5·1. $C_{15}H_{14}O_5$ requires C, 65·7; H, 5·0%.)

The acetyl derivative prepared in the usual manner crystallised from alcohol in white needles, m.p. 185°. (Found: C, 64·7; H, 5·2. $C_{17}H_{16}O$ requires C, 64·6; H, 5·1%.)

7-Hydroxy-6-carboxy-3: 4-cyclohexeno-coumarin obtained by the cold alkaline hydrolysis of the above coumarin crystallised from alcohol in minute needles, m.p. 263° (Decomp.). The same coumarin could be obtained by condensing β-resorcylic acid with ethyl cyclo-hexanone-2-carboxylate in presence of 73 per cent. sulphuric acid. Its alcoholic solution gave brown-red coloration with ferric chloride. When heated above its m.p. (250–60°) for one hour, the acid decomposed giving 7-hydroxy-3: 4-cyclohexeno-coumarin, identified by comparison with an authentic specimen. (Found: C, 64·3; H, 4·6. $C_{14}H_{12}O_5$ requires C, 64·6; H, 4·6%.)

7-Hydroxy-8-acetyl-3: 4-cyclohexeno-coumarin was obtained by heating an intimate mixture of 7-acetoxy-3: 4-cyclohexene-coumarin (1 g.), anhydrous aluminium chloride (2 g.) at 140°–50° for one hour. It crystallised from alcohol in fine needles, m.p. 172°, and its alcoholic solution gave reddish violet coloration with ferric chloride. (Found: C, 69·6; H, 5·4. $C_{15}H_{14}O_4$ requires C, 69·8; H, 5·4%.)

The *acetyl* derivative crystallised from alcohol in lustrous needles, m.p. 224°. (Found: C, 67·8; H, 5·4. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%.)

5-Hydroxy-6-acetyl-3: 4-cyclohexeno-coumarin was prepared by heating the solution of resacetophenone (1·8 g.), the keto-ester (2 g.) and aluminium chloride (3·5 g.) in nitrobenzene (30 c.c.) at 110–15° for 1½ hours, and worked up as usual. The brown solid crystallised from alcohol in pale-yellow needles, m.p. 202° (yield, 2·5 g.). Its alkaline solution was yellow and non-fluorescent, while its alcoholic solution gave reddish-violet coloration with ferric chloride. (Found: C, 69·5; H, 5·2. $C_{15}H_{14}O_4$ requires C, 69·8; H, 5·4%.)

The *acetyl* derivative crystallised from alcohol in small needles, m.p. 124–25°. (Found: C, 68·1; H, 5·2. $C_{17}H_{16}O_5$ requires C, 68·0; H., 5·3%.)

(B) Coumarins from ethyl cyclopentanone-2-carboxylate 7-hydroxy-6-carbomethoxy-3 : 4-cyclo-penteno-coumarin was obtained from methyl β-resorcylate (2 g.), ethylcyclopentanone carboxylate (2 g.) and 73 per cent. sulphuric acid (20 c.c.) (yield, 1·3 g.). It crystallised from alcohol in needles m.p. 223. The use of aluminium chloride or phosphorous oxychloride as a condensing agent gave the same coumarin. Its alcoholic solution gave faint violet coloration with ferric chloride. (Found : C, 64·2; H, 4·2. $C_{14}H_{12}O_5$ requires C, 64·6; H, 4·6%.)

The *acetyl* derivative crystallised from alcohol in lustrous needles, m.p. 182–83°. (Found: C, 63·4; H, 4·6. $C_{16}H_{14}O_6$ requires C, 63·6; H, 4·6%.)

7-Hydroxy-6-carboxy-3 : 4-cyclo-penteno-coumarin crystallised from alcohol in tiny needles, m.p. 261° (decomp.). Its alcoholic solution gave deep reddish violet coloration with ferric chloride. (Found: C, 63·2; H, 4·2. $C_{13}H_{10}O_5$ requires C, 63·4; H, 4·1%.)

On decarboxylation, the acid gave 7-hydroxy-3 : 4-cyclo-penteno-coumarin, m.p. 242°, undepressed by comparison with an authentic specimen.

The *phenyl ester* was obtained by heating the coumarin acid (0·1 g.), phenol (2 g.) and acetic anhydride on sand-bath for three hours, and crystallised from alcohol in needles, m.p. 160–61°. (Found: C, 71·0; H, 4·5. $C_{19}H_{14}O_5$ requires C, 70·8, ; H, 4·3%.)

7-Hydroxy-8-acetyl-3 : 4-cyclopenteno-coumarin was obtained by heating an intimate mixture of 7-acetoxy-3 : 4-cyclopenteno-coumarin (1 g.), and aluminium chloride (2 g.) as usual, and crystallised from alcohol in needles, m.p. 154°. (Found: C, 68·6; H, 5·0. $C_{14}H_{12}O_4$ requires C, 68·8; H, 4·9%.)

The *acetyl* derivative crystallised from alcohol in needles, m.p. 219–20°. (Found: C, 67·0; H, 4·8. $C_{16}H_{14}O_5$ requires C, 67·1; H, 4·9%.)

7-Hydroxy-6-acetyl-3 : 4-cyclopenteno-coumarin was obtained by heating a solution of resacetophenone (2 g.), the keto-ester (2 g.), and phosphorous oxychloride (2 c.c.) in dry benzene (20 c.c.), on water-bath for two hours. The benzene extract left a solid which crystallised from alcohol in clusters of needles, m.p. 247 (yield, 25 per cent.). Its alcoholic solution gave reddish violet coloration with ferric chloride. Its alkaline solution gave blue fluorescence. (Found: C, 68·5; H, 5·1. $C_{14}H_{12}O_4$ requires C, 68·8; H, 4·9%.)

The *acetyl derivative* crystallised from alcohol in needles, m.p. 162°. (Found: C, 66·8; H, 5·0. $C_{16}H_{14}O_5$ requires C, 67·1; H, 4·9.)

5-Hydroxy-6-acetyl-3 : 4-cyclopenteno-coumarin was obtained from resacetophenone (2 g.), the keto-ester (2 g.), aluminium chloride (3·5 g.) and nitrobenzene (30 c.c.) in the usual manner and crystallised from benzene in pale-yellow needles, m.p. 192°. Its yellow alkaline solution was devoid of fluorescence. (Found: C, 68·5; H, 5·0. $C_{14}H_{12}O_4$ requires C, 68·8; H, 4·9%.)

The *acetyl* derivative crystallised from alcohol in needles, m.p. 116–17°. (Found: C, 66·9; H, 5·2. $C_{16}H_{14}O_5$ requires C, 67·1; H, 4·9%.)

(*C*). *Coumarins from ethyl-4-methyl-cyclopentanone-2-carboxylate, 7-Hydroxy-6-carbo-methoxy-3 : 4-(4′-methyl-cyclopenteno-coumarin* obtained as usual from methyl β-resorcylate (2 g.), the keto-ester (2 g.) and 73 per cent. sulphuric acid (20 c.c.) crystallised from alcohol in needles, m.p. 168° (yield, 1·5 g.). (Found: C, 65·5; H, 5·2. $C_{15}H_{14}O_5$ requires C, 65·7; H, 5·0%.)

The *acetyl* derivative crystallised from alcohol in needles, m.p. 132°. (Found: C, 64·5; H, 5·1. $C_{17}H_{16}O_6$ requires C, 64·6; H, 5·1%.)

7-Hydroxy-6-carboxy-3 : 4-(4-methyl-cyclopenteno)-coumarin prepared from β-resorcylic acid crystallised from alcohol in needles, m.p. 243–44° (decomp.). On decarboxylation, it gave 7-hydroxy-3 : 4-(4′-methyl cyclopenteno-coumarin, m.p. 176°. The alkaline solutions of the coumarin ester as well as the acid gave blue fluorescence, and their alcoholic solutions gave reddish violet coloration with ferric chloride. (Found: C, 64·4; H, 4·7. $C_{14}H_{12}O_5$ requires C, 64·6; H, 4·6%.)

8-Acetyl-7-hydroxy-3 : 4-(4′-methyl-cyclopenteno)-coumarin was obtained by heating the intimate mixture of 7-acetoxy-coumarin (1 gm.) and aluminium chloride (2 g.) as usual, and crystallised from alcohol in needles, m.p. 118° Its alcoholic solution gave reddish violet, coloration. (Found: C, 69·6; H, 5·4. $C_{15}H_{14}O_4$ requires C, 69·8; H, 5·4%.)

The *acetyl* derivative crystallised from alcohol in needles, m.p. 182°. (Found: C, 67·9; H, 5·4. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%.)

5-Hydroxy-8-acetyl-3 : 4-(4′-methyl-cyclopenteno)-coumarin was obtained from the keto-ester (2 g.), resacetophenone (2 g.), aluminium chloride (3·5) and nitrobenzene (30 c.c.) as usual, and crystallised from benzene in small needles, m.p. 154–55° (depressed to 123° by resacetophenone). Its yellow alkaline solution was non-fluorescent, while its alcoholic solution gave reddish violet coloration with ferric chloride. (Found : C, 69·5; H, 5·5. $C_{15}H_{14}O_4$ requires C, 69·8; H, 5·4%.)

The *acetyl* derivative crystallised from dilute alcohol in needles, m.p. 69–70°. (Found: C, 68·1; H, 5·4. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%.)

Summary

Coumarins have been prepared from ethyl-β-resorcylate and resacetophenone by condensing them with cylic β-ketonic esters like ethyl cyclohexanone-2-carboxylate, ethyl cyclo-pentanone-2-carboxylate and ethyl-4-methyl-cyclopentanone-2-carboxylate in presence of 73 per cent. sulphuric

acid, phosphorous oxychloride and anhydrous aluminium chloride as condensing agents. Only 7-hydroxy coumarins were obtained in the case of methyl β-resorcylate, while resacetophenone gave 7-hydroxy-coumarins in presence of phosphorous oxychloride, but 5-hydroxy coumarins with aluminium chloride.

References

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2. Shah and co-workers .. *J. C. S.*, 1938, 228, 1066, 1414, 1939, 1250.
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4. W. Baker and co-workers .. *Ibid.*, 1934, 1684, 1935, 479, 628, 1937.

HETEROCYCLIC COMPOUNDS

Part XIX. The Kostanecki Acetylation of γ-Orcpropiophenone and γ-Orcbutyrophenone and Formation of 5-Hydroxy-2:3:7-Trymethyl-chromone and 5-Hydroxy-2:7-Dimethyl-3-Ethyl-Chromone

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Desai and Vakil[1] found that the Kostanecki acetylation of γ-orcacetophenone gave exclusively the chromone, while Sethna and Shah[2] observed that the same reaction gave exclusively the coumarin in the case of β-orcacetophenone. As the two isomeric hydroxy-ketone differed widely in their behaviour, it was thought interesting to submit other inaccessible γ-acyl-orcinol. which became available as the result of a method described by the authors.[3]

The vigorous acetylation of γ-orcpropiophenone gave a mixture of two products, alkali-soluble and alkali-insoluble. As the alkali-soluble product gave deep violet coloration with ferric chloride and *p*-orsellinic acid on alkaline hydrolysis, it should be 5-hydroxy-2: 3: 7-trimethyl-chromone (I) while the other product was its 5-acetoxyderivative, as it gave (I) after deacetylation on keeping in contact with concentrated sulphuric acid.

Similarly γ-orcbutyrophenone reacted with acetic anhydride giving 5-hydroxy-2: 7-dimethyl-3-ethyl-chromone. Thus it is observed that the Kostanecki acetylation of γ-acyl-orcinols leads to the exclusive formation of chromones.

Experimental

Acetylation of γ-orcpropiophenone and formation of 5-hydroxy-2: 3: 7-trimethyl-chromone and 5-acetoxy-2: 3: 7-trimethyl chromone.

A mixture of 2-propionyl-5-methyl resorcinol (5 g.) anhydrous sodium acetate (10 g.) and acetic anhydride (50 c.c.) was heated in an oil-bath at 180–190° for sixteen hours. The clear solution was poured into a large quantity of water and kept overnight to decompose the excess of acetic anhydride. The oily layer which separated out at the start gradually solidified, and the dry crude solid melted indefinitely at 82–86° (yield, 3·5 gm.). Much of the crude solid dissolved in 5% sodium hydroxide solution, and the solid recovered on acidification with concentrated hydrochloric acid crystallised from dilute alcohol in clusters of colourless needles, m.p. 109–110°. It was soluble in the usual organic solvents, while its solution in

alkali as well as concentrated sulphuric acid was yellow and non-fluorescent. Its alcoholic solution gave deep-violet coloration with ferric chloride. Therefore, the compound was *5-hydroxy-2: 3: 7-trimethyl-chromone*. (Found: C, 70·5; H, 6·0. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9%.)

The alkali insoluble product crystallised from dilute alcohol in needles, m.p. 112–113° (depressed to 89–90° by admixture with the foregoing compound). Its alcoholic solution did not give any coloration with ferric chloride. (Found: C, 68·0; H, 5·6. $C_{14}H_{14}O_4$ requires C, 68·2; H, 5·7%.)

The solution of the substance (0·5 g.) in concentrated sulphuric (10 c.c.) was kept overnight, and poured into water. The solid crystallised from dilute alcohol in needles, m.p. 109–10° C. (depressed to 85–88° by the original substance).

Hydrolysis of 5-hydroxy-2: 3: 7-trimethyl-chromone to p-orsellinic acid.

A solution of the chromone (0·3 g.) in 5 per cent. sodium hydroxide (20 c.c.) was refluxed on a sand-bath for two hours. The acid obtained on acidification with concentrated hydrochloric acid crystallised from dilute alcohol in needles, m.p. 164–165°, and its alcoholic solution gave blue coloration with ferric chloride. It was identified as *p*-orsellinic acid by comparison with an authentic specimen.

Acetylation of γ-orcbutyrophenone, and formation of 5-hydroxy-2: 7-dimethyl-3-ethyl-chromone.

The reaction was carried out as above, and worked up as usual. The solid which was soluble in 5 per cent. sodium hydroxide crystallised from dilute alcohol in needles, m.p. 78-79°. Its alcoholic solution gave deep violet coloration with ferric chloride. It gave yellow and non-fluorescent solution with dilute alkali and concentrated sulphuric acid, and *p*-orsellinic acid, on alkaline hydrolysis. (Found: C, 71·5; H, 6·6. $C_{13}H_{14}O_3$ requires C, 71·5; H, 6·4%.)

We are thankful to Rev. Father A. M. Coyne, S.J., for his kind interest in this work.

Summary

The Kostanecki acetylation of 2-propionyl-5-methyl and 2-butyryl-5-methyl resorcinols gave exclusively the chromones.

References

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2. Sethna and Shah .. *J. Ind. Chem. Soc.*, 1940, **17**, 239, 487.
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HETEROCYCLIC COMPOUNDS

Part XX. The Kostanecki Acylation of Quinacetophenone, Quinbenzophenone and γ-Orcacetophenone, and Synthesis of 6-Hydroxy and 5-Hydroxy Chromones and Coumarins

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During the last twenty years, a considerable amount of work has been published on the limited applicability of the Kostanecki Reaction by various workers,[1] and the conclusion has been drawn that this reaction may give either chromones, or the coumarins or the mixture of both and depends not only on the nature of the acid anhydrides and the salts used but also on the nature of the O-hydroxyarylmethyl ketone.

We thought it worth while to subject quinacetophenone and quinbenzophenone to this reaction in order to see how far it can be used as a method for the synthesis of 6-hydroxy-chromones and coumarins, the number of which is very scanty. Thus some 6-hydroxy-flavones have been described by Chadha and Venkataraman,[2] while Borche[3] has described the synthesis of three 6-hydroxy coumarins.

Quinacetophenone gave only 6-acetoxy-3-acetyl-2-methyl chromone on heating with acetic anhydride and sodium acetate, while propionic anhydride and sodium propionate gave a mixture of 6-hydroxy-3-propionyl-2-ethylchromone and 6-hydroxy-3:4-dimethyl coumarin approximately in 3:2 proportion. Similarly butyric anhydride and sodium butyrate gave 6-hydroxy-3-butyryl-2-methyl-chromone and 6-hydroxy-4-methyl-3-ethyl coumarin in almost the same proportion. Quinbenzophenone reacted with acetic anhydride and sodium acetate giving 6-acetony-4-phenyl coumarin (excellent yield) and this constitutes a convenient method of preparing 6-hydroxy-4-phenyl coumarins, as the Pechmann condensation between hydroquinone and ethyl benzoylacetate does not take place.

In light of the recent interesting observations of Sethna and Shah (*loc. cit.*) that β-orcacetophenone gave exclusively the coumarins on heating with fatty acid anhydrides and their salts, and of Desai and (Miss) Vakil[4] that γ-orcacetophenone gave only the chromone with acetic anhydride and sodium acetate, it was interesting to see its behaviour on heating with other

acid anhydrides in presence of their sodium salts. γ-Orcacetophenone, on heating with propionic anhydride and sodium propionate, gave a mixture of 2-ethyl-3-propionyl-5-hydroxy-7-methyl chromone and 3:4:7-trimethyl-5-hydroxy-coumarin, approximately in proportions of 2:1, while the mixture of 2-propyl-3-butyryl-5-hydroxy-7-methyl chromone and 3-ethyl-4:7-dimethyl-5-hydroxy-coumarin in almost the same proportion was obtained on heating γ-orcacetophenone with butyric anhydride and sodium butyrate. Finally benzoic anhydride and sodium benzoate gave 2-phenyl-3-benzoyl-5-hydroxy-7-methyl-chromone.

These results support the observations of Heilbron and co-workers (*loc. cit.*) and emphasise the limited character of the Kostanecki Reaction for the chromone formation.

Experimental

Quinacetophenone was prepared by the Fries migration of hydroquinone diacetate. The following method gave the best yield of this ketone as it is dependent upon temperature and the amount of aluminium chloride used.

An intimate mixture of hydroquinone diacetate (14 g.) and aluminium chloride (28 g.) was heated in an oil-bath at 195–200° for one hour and a half hour, cooled, and decomposed with ice-cold water. The solid crystallised from dilute alcohol in needles, m.p. 202° (yield = 10 g.).

6-*Acetoxy*-3-*acetyl*-2-*methyl chromone*.—A mixture of quinacetophenone (5 g.), sodium acetate (10 g.) and acetic anhydride (35 c.c.) was heated at 200–210° for twelve hours and poured into water. The solid crystallised from dilute alcohol in colourless needles, m.p. 125° (yield = 3 gm.). (Found: C, 64·4; H, 4·8. $C_{14}H_{12}O_5$ requires C, 64·6; H, 4·6 per cent.)

6-*Hydroxy*-3-*acetyl*-2-*methyl-chromone* was obtained by pouring the solution of the *acetoxy chromone* in 85 per cent. sulphuric acid on ice after three hours and crystallised from alcohol in thick needles, m.p. 221°. Its solution in alkali as well as concentrated sulphuric acid was yellow and non-fluorescent. (Found: C, 65·9; H, 4·7. $C_{12}H_{10}O_4$ requires C, 66·0; H, 4·6 per cent.)

The above conversion of *acetoxy-chromone* into *hydroxy-chromone* can also be effected by heating (1 g.) with aluminium chloride (3 g.) at 180° for two hours.

6-*Hydroxy*-γ-*methylchromone*.—The above chromone (1 g.) was heated with 5 per cent. sodium carbonate solution (20 c.c.) on a sand-bath for two hours. The filtered solution on acidification with concentrated hydrochloric

acid gave a solid which crystallised from dilute alcohol in colourless, lustrous needles, m.p. 245°. Its solution in alkali as well as concentrated sulphuric acid was yellow and non-fluorescent. (Found: C, 67·9; H, 4·6. $C_{10}H_6O_3$ requires C, 68·2; H, 4·5 per cent.) Similar hydrolysis of the above chromone with sodium hydroxide solution gave 2:5-dihydroxy-benzoic and m.p. 196° (undepressed by admixtures with an authentic specimen).

6-Hydroxy-3-propionyl-2-ethyl-chromone and 6-hydroxy 3:4-dimethyl-coumarin.—

The mixture of quinacetophenone (5 g.), sodium propionate (10 g.) and propionic anhydride (35 c.c.) was heated at 200–10° for 12 hours. The pasty mass obtained by pouring into water was kept in contact with 85 per cent. sulphuric acid, overnight, as it showed no tendency to crystallise from any solvent, and poured into water. The solid thus obtained was treated with benzene. The benzene-soluble product crystallised from dilute alcohol in needles, m.p. 151°, and was identified as *6-hydroxy-3-propionyl-2-ethyl-chromone* as it gave 2:5-dihydroxy benzoic acid on alkaline hydrolysis (yield = 1·5 g.) (Found: C, 68·1; H, 5·8. $C_{14}H_{14}O_4$ requires C, 68·3; H, 5·7 per cent.)

The *benzene-insoluble* product crystallised from alcohol in pale-yellow needles, m.p. 241°, and was identified as 3:4-dimethyl-6-hydroxy-coumain with an authentic specimen (yield = 1·0 g.). The coumarin underwent nitration readily by the addition of finely powdered sodium nitrate (0·8 g.) to its solution in concentrated sulphuric acid (1·0 g. in 20 c.c.). After keeping the mixture overnight the yellow product obtained by pouring the mixture over ice-cold water crystallised from alcohol in yellow flakes, m.p. 213°, and was probably the 5-nitro-derivative. (Found: N, 5·9. $C_{11}H_9O_5N$ requires N, 6·0 per cent.)

6-Hydroxy-3-butyryl-2-propyl-chromone and 6-hydroxy-4-methyl-3-ethyl-coumarin.—The mixture of quinacetophenone (5 g.), sodium butyrate (12·5 g.) and butyric anhydride (40 c.c.) was heated at 220–30° for 18 hours. As the pasty mass did not solidify, it was kept in contact with 85 per cent. sulphuric acid overnight and poured into water. The solid was treated with benzene, and the *benzene*-soluble product crystallised from dilute alcohol in pale-yellow needles, m.p. 151° (depressed to 120–25° by 3-propionyl-2-ethyl-6-hydroxy chromone which has curiously the same m.p.) (yield = 1·5 g.). It gave 2:5-dihydroxybenzoic acid on alkaline hydrolysis. (Found: C, 69·8; H, 96·7. $C_{16}H_{18}O_4$ requires C, 70·0; H, 6·6 per cent.)

The *benzene-insoluble* product crystallised from dilute alcohol in pale yellow needles, m.p. 211°, and was identified as 6-hydroxy-4-methyl-3-ethyl coumarin, by comparing with a specimen prepared by condensing ethyl ethylaceto-acetate with hydroquinone in presence of aluminium chloride (yield = 1·0 g.). (Found: C, 70·3; H, 6·1. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9 per cent.)

Quinbenzophenone was obtained by the Fries migration of hydroquinone dibenzoate and melted at 125°.

6-*Acetoxy*-4-*phenyl-coumarin* was obtained by heating the mixture of quinbenzophenone (5 g.), sodium acetate (10 g.) and acetic anhydride (35 c.c.) at 210-20° for twelve hours, and crystallised from dilute acetic acid in colourless, lustrous needles, m.p. 162° (yield = 4 gm.). (Found: C, 72·9; H, 4·5. $C_{17}H_{14}O_4$ requires C, 72·9; H, 4·3 per cent.)

6-*Hydroxy*-4-*phenyl coumarin* was obtained by deacetylating the above coumarin with 85 per cent. sulphuric acid or aluminium chloride, and crystallised from alcohol in pale-yellow needles, m.p. 242–43°. (Found: C, 75·4; H, 4·3. $C_{15}H_{10}O_3$ requires C, 75·6; H, 4·2 per cent.)

The *dibromo derivative* crystallised from alcohol in pale-yellow needles, m.p. 217°. (Found: Br, 40·1. $C_{15}H_8O_3Br_2$ requires Br, 40·4 per cent.

B. Kostanecki Reaction with γ-Orcacetophenone.

The most convenient method of preparing γ-orcacetophenone is the deacetylation of 2:4-diacetyl-orcinol, which can be prepared by the Fries migration of orcinol diacetate. The method which is general, is described as follows:—

A mixture of orcinol diacetate (16 g.) and aluminium chloride is heated at 145–55° for 1·5 hours, and decomposed with ice-cold water. The crude solid (7 g.) which is a mixture of 2:4-diacetylorcinol, β-orcacetophenone and γ-orcacetophenone was dissolved in 85 per cent. sulphuric acid (75 c.c.) the mixture was poured over ice after four hours. The resulting solid (5 g.) was almost pure γ-orcacetophenone, and crystallised from dilute alcohol in needles, m.p. 146°.

Propionylation of γ-orcacetophenone and formation of 5-hydroxy-7-methyl-3-propionyl-2-ethyl-chromone and 5-hydroxy-3:4:7-trimethyl coumarin.

The mixture of γ-orcacetophenone (5 g.), propionic anhydride (35 c.c.) and sodium propionate (10 g.) was heated at 200–10° for 18 hours, and the pasty mass obtained after pouring the mixture into water was dissolved in 85 per cent. sulphuric acid. The solid obtained by pouring the solution

over ice after 4 hours was treated with petrol (b.p. 60–80°), which dissolved a considerable portion of it, and on recrystallisation from the same solvent long, stout needles, m.p. 99–100° were obtained (1·5 g.). Its alcoholic solution gave deep violet coloration with ferric chloride, and as it gave *p*-orsellinic acid on alkaline hydrolysis it was identified as *5-hydroxy-7-methyl-3-propionylchromone*. Its yellow, alkaline solution was devoid of fluorescence. (Found: C, 69·0; H, 6·5. $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·2 per cent.)

The petrol-insoluble product (0·75 g.) crystallised from alcohol in cubes, m.p. 250°, and was identified as 5-hydroxy-3: 4: 7-trimethyl-coumarin by comparison with an authentic specimen prepared by Chakravarti's method.[5] The *acetyl* derivative (m.p. 135°) of this coumarin underwent Fries migration giving 6-acetyl-5-hydroxy-3: 4: 7-trimethyl coumarin, which crystallised from alcohol in needles, m.p. 166°. Its alcoholic solution gave red coloration with ferric chloride. (Found : C, 68·1; H, 5·9. $C_{14}H_{14}O_4$ requires C, 68·3; H, 5·7 per cent.)

Butyrylation of γ-Resacetophenone, and formation of 5-hydroxy-7-methyl-3-butyryl-3-propyl-chromone and 5-hydroxy-4: 7-dimethyl-3-ethyl coumarin.

The mixture of γ-orcacetophenone (5 g.), sodium butyrate (12·5 g.) and butyric anhydride (40 c.c.) was heated at 210–20° for 18 hours, and poured into water. The viscous mass was dissolved in 85 per cent. sulphuric acid, and worked up after 4 hours. The petrol-soluble (60–80° b.p.) portion crystallised from light petrol (b.p. 40–60°) in thick needles, m.p. 95–96° (yield = 0·8 g.). Its alcoholic solution gave deep violet coloration with ferric chloride and as its alkaline hydrolysis gave *p*-orsellinic acid, it was identified as 5-hydroxy-7-methyl-3-butyryl-2-propyl chromone. (Found: C, 70·5; H, 6·8. $C_{17}H_{20}O_4$ requires C, 70·8; H, 6·9 per cent.)

The *petrol-insoluble* portion crystallised from alcohol in needles, m.p. 205-06° and was identified as 5-hydroxy-3-ethyl-4: 7-dimethyl coumarin by comparison with an authentic specimen prepared by Chakravarti's method (*loc. cit.*) (yield = 0·4 g.).

Benzoylation of γ-orcacetophenone and formation of 5-hydroxy-3-benzoyl-7-methyl-flavone.

A mixture of γ-orcacetophenone (2·5 g.), sodium benzoate (7·5 g.) and benzoic anhydride (25 g.) was heated at 200–10° for 20 hours. The resulting mass was alternately treated with petrol (b.p. 60–80), and water, the residue dissolved in concentrated sulphuric acid, and poured into water

after 4 hours. The solid, after the removal of benzoic acid with sodium bicarbonate solution crystallised from alcohol in colourless needles, m.p. 143° (yield = 0·75 g.). In alcoholic solution gave deep violet coloration with ferric chloride while its alkaline hydrolysis gave *p*-orsellinic acid. (Found: C, 77·3; H, 4·7. $C_{23}H_{16}O_4$ requires C, 77·5; H, 4·5 per cent.)

We take this opportunity of expressing our thanks to Rev. Father A. M. Coyne, S.J., for the kind interest in this work and provision of facilities.

Summary

The propionylation as well as butyrylation of quinacetophenone gave a mixture of chromones and coumarins, while its acetylation gave only the chromone. Similarly the acetylation of quinbenzophenone gave the coumarin. Thus coumarins which cannot be obtained by the Pechmann method can be readily prepared by this method. Similarly propionylation and butyrylation of γ-orcacetophenone gave the mixture of chromones and coumarins, while the benzoylation gave the flavone.

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STUDIES IN NAPHTHALENE SERIES

Part XV. The Preparation and Properties of 4-Phenylacetyl-1-Naphthol and 2-Phenylacetyl-1-Naphthol

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The condensation of α-naphthol with phenylacetyl chloride gave a mixture of 4-phenylacetyl- and 2-phenyl-acetyl-1-naphthols, the latter being in preponderant amount. As the yield of the 4-isomer was not good, the Fries migration of 1-naphthyl phenylacetate was tried, but this method also gave a poor yield. The condensation of methoxy naphthalene gave a good yield of 4-phenylacetyl-1-methoxy naphthalene, but attempts to demethylate it by hydrogen bromide, hydrogen iodide and anhydrous aluminium chloride were not successful. As only a small quantity of 4-phenylacetyl-1-naphthol was available, only its bromination was studied.

As considerable quantity of 2-phenylacetyl-1-naphthol was formed, we undertook its reduction, bromination, nitration, and bromination of the chromone prepared by Cheema and Venkataraman by its vigorous acetylation.

Experimental

4-Phenylacetyl-1-naphthol

To a solution of α-naphthol (20 g.) in nitrobenzene (60 c.c.) containing finely powdered anhydrous zinc chloride (20 g.) in suspension, the solution of phenylacetyl chloride (40 g.) in nitrobenzene (40 c.c.) was gradually added. After allowing the mixture to stand at the room temperature for 24 hours, it was decomposed by ice-cold hydrochloric acid, and the nitrobenzene removed by steam. The brown solid that was obtained was alternately extracted with water (thrice) and 5 per cent. sodium carbonate solution remove α-naphthol and phenylacetic acid. The residue on extraction with 5 per cent. sodium hydroxide solution left an insoluble solid, and the alkaline extract on acidification with hydrochloric acid gave the product most of which went in solution when treated with petroleum ether (b.p. 60–80°). The insoluble product crystallised from alcohol in brownish red needles, m.p. 92–93° (yield 5%). Its alcoholic solution gave an intense red coloration with ferric chloride. (Found: C, 82·6; H, 5·3; $C_{18}H_{14}O_2$ requires C, 82·4; H, 5·3 per cent.)

The petroleum-ether soluble product crystallised in small white needles, m.p. 100–01° C. This was identified as 2-phenyl-acetyl-1-naphthol (yield 10%).

The alkali-insoluble product was crystallised from chloroform and acetic acid mixture, m.p. 130–32° C. Its alcoholic solution gave green coloration with ferric chloride. This was probably 2-4 diphenyl acetyl-1-naphthol.

The Fries migration of 1-*naphthol-phenyl acetate. Preparation of* 1-*naphthol-phenyl-acetate.*—1-Naphthol (50 g.) dissolved in sodium hydroxide (10%; 500 c.c.) and phenylacetyl chloride (60 g.) was very gradually added with constant shaking to the ice-cooled alkaline solution. The mixture was shaken well and kept for four hours and poured in water. The product on washing and crystallising through acetic acid gave small colourless plates, m.p. 46–47° C.

4-*Phenyl-acetyl*-1-*naphthol.*—An intimate mixture of dry 1-naphthol-phenylacetate (10 g.) and anhydrous aluminium chloride (25 g.) was heated in an oil-bath at 150° C. for one hour. The reaction mixture was decomposed in the cold, and the product on treatment with alkali gave alkali-soluble and insoluble substances.

The alkali-soluble material was acidified and the brownish product was treated with petroleum-ether (b.p. 60–80° C). The soluble portion crystallised in white needles, m.p. 100–01° C. undepressed by 2-phenyl-acetyl-1-naphthol (yield 5 per cent.).

The petrol-insoluble product was crystallised from alcohol in short needles, m.p. 92–93° C. undepressed by 4-phenyl-acetyl-1-naphthol (yield 5 per cent.).

2:4-*Dinitrophenyl-hydrazone of* 4-*phenyl-acetyl*-1-*naphthol.*—The ketone (0·5 g.) was dissolved in glacial acetic acid (10 c.c.) and 2:4-dinitrophenyl-hydrazine (0·5 g.) dissolved in glacial acetic acid (10 c.c.) was added and the mixture was heated under reflux for six hours. On cooling the product crystallised in small red needles, m.p. 177-78°. (Found: N, 12·6. $C_{24}H_{18}O_5N_4$ requires N, 12·7 per cent.)

Condensation of 1-*naphthyl methyl ether with phenylacetyl chloride by Friedel and Crafts method.*

Preparation of 1-*methoxy*-4-*phenyl acetyl-naphthalene.*—1-Naphthyl-methyl ether (10 c.c.) dissolved in dry benzene (20 c.c.) and phenyl acetyl-chloride (18 g.) dissolved in dry benzene (20 c.c.) were alternately added with constant shaking, to a cooled suspension of powdered anhydrous zinc chloride (10 g.) in dry nitrobenzene (30 c.c.). After keeping the reaction

at room temperature for 24 hours, it was decomposed by dilute hydrochloric acid in the cold. The nitrobenzene was steam-distilled and the product was purified and crystallised from alcohol in long white needles, m.p. 80–81° C. Its alcoholic solution gave no coloration with ferric chloride. (Found: C, 82·5; H, 5·6; $C_{19}H_{16}O_2$ requires C, 82·6; H, 5·8 per cent.)

Demethylation of 1-methoxy-4-phenyl acetyl naphtholene by hydrogen bromide and pydriodic acid in glacial acetic acid also by anhydrous aluminium chloride.—Demethylation of 1-methoxy-4-phenyl acetyl naphthalene by 50% hydrogen bromide was carried out for 8 hours and only the original product was obtained.

The demethylation of this compound was tried with 50% hydrogen iodide without any success. Heating the methoxy product (3 gm.) with anhydrous aluminium chloride in dry benzene (50 c.c.) for one hour gave phenyl-acetic acid.

Bromination of 4-phenylacetyl-1-naphthol with one mol. of bromine: Preparation of 2-bromo-phenyl-acetyl-1-naphthol.—4 Phenyl-acetyl-1-naphthol (0·4 gm.) was dissolved in glacial acetic acid (10 c.c.) to which a solution of bromine (0·15 c.c.) in glacial acetic acid (5 c.c.) was added drop by drop with constant shakings. The reaction mixture was kept for 24 hours and then poured into large quantity of ice-cold water. The red substance which separated out was crystallised from alcohol in long red needles m.p. 76–78° C., and was unaffected by heating with 10 per cent. alkali. (Found: Br, 11·50. $C_{18}H_{13}O_2$ Br requires Br 11·7 per cent.)

Derivatives of 2-phenylacetyl-1-naphthol-4-nitrophenylhydrazone.

This was prepared by heating the mixture of the ketone (0·5 gm.) and 4-nitrophenyl-hydrazine (0·5) in alcohol (25 c.c.) for 6 hours, and crystallised from alcohol in short, orange-red needles m.p. 249–50° C. (Found: N, 10·8. $C_{24}H_{19}O_3N_3$ requires N, 10·6 per cent.)

The 2:4-dinitrophenyl-hydrazone crystallised from alcohol in small, orange-red needles, m.p. 275–77°. (Found: N, 12·5. $C_{24}H_{18}O_5N_4$ requires N, 12·7 per cent.)

Bromination of 2-phenyl acetyl-1-naphthol with one mol. of bromine: Preparation of 4-bromo-2-phenyl acetyl-1-naphthol.—The ketone (1 gm.) was dissolved in acetic acid (20 c.c.) and to this, a solution of bromine (0·25 c.c.) in acetic acid (5 c.c.) was added drop by drop with constant shaking. The mixture was kept for 24 hours and then poured in water. The yellow substance that separated out was crystallised from alcohol in

yellow needles m.p. 97–98° C. (depressed to 72° C. by the original ketone). (Found: Br, 11·9. $C_{18}H_{13}O_2$ Br, requires Br, 11·8 per cent.)

Bromination of 2-phenyl acetyl-1 naphthol with two and three mols. of bromine gave only 4-bromo-2-phenyl acetyl α-naphthol. The bromo product was unaffected by heating with 10 per cent. alkali.

Nitration of 2-phenyl acetyl-1-naphthol with one mol. of fuming nitric acid: Preparation of 4-nitro-2-phenyl-acetyl-1-naphthol.—To the solution of the ketone (2 gm.) in acetic acid (30 c.c.) a solution of fuming nitric acid (d. = 1·5; 0·4 c.c.) in acetic acid (5 c.c.) was added drop by drop with constant shaking and the mixture was kept for 24 hours at room temperature. It was poured in water and the product was crystallised from alcohol in orange yellow needles m.p. 156–157° C. (Found: N, 4·3; $C_{18}H_{13}O_4N$, requires N, 4·6 per cent.)

Nitration of 2-phenylacetyl-1-naphthol with two and three mols of fuming nitric acid gave only the mono nitroderivative.

Clemmensen Reduction of 2-phenyl-acetyl-1-naphthol: Preparation of 2-(β-phenyl-ethyl)-1-naphthol.—A mixture of 2-phenyl acetyl-1-naphthol (2 gm.) amalgamated zinc (7 gm.) and hydrochloric acid (1 : 1; 60 c.c.) was heated on sand-bath under reflux for 20 hours.

On neutralizing the alkaline solution, a brownish product was obtained which was crystallised from alcohol in yellow needles, m.p. 106–107°C. This alcoholic solution gave no coloration with ferric chloride. (Found C, 86·9; H, 6·4; $C_{18}H_{16}O$ requires C, 87·1; H, 6·5 per cent.)

Formation of 2-(β-phenyl-ethyl)-ac-tetrahydro-1-naphthol.—On evaporation, the ethereal layer gave the neutral hydroxylic compound which was crystallised from alcohol in *white shining needles,* m.p. 196–98° C. Its alcoholic solution gave no coloration with ferric chloride. (Found: C, 85·9; H, 8·05; $C_{18}H_{20}O$ requires C, 85·71; H, 7·9 per cent.)

Kostanecki Reaction with 2-phenyl-acetyl-1-naphthol: Preparation of 2-methyl-3-phenyl-1 : 4-α-naphthopyrone.—The ketone (3 gm.) was heated with acetic anhydride (25 c.c.) and sodium acetate (3 gm.) in an oil-bath at 180–90° C. for eight hours. The mixture was poured in water and separated solid was purified and crystallised from alcohol in pale yellow needles m.p. 210–11° C. (Venkataraman and Cheema give 204°). It was soluble in the usual organic solution. (Found: C, 84·0; H, 4·7; call. for $C_{20}H_{12}O_2$ C, 83·9, H, 4·9 per cent.)

Hydrolysis of the above pyrone.—The above pyrone (0·2 gm.) was refluxed on water for three hours with caustic soda (10%, 15 c.c.). On

acidifying the alkaline solution pale yellow substance was obtained which was soluble in 5% sodium-bicarbonate solution. This was crystallised from alcohol, m.p. 186–87° C., undepressed by 1-hydroxy-2-naphthoic acid.

Bromination of the pyrone with one mol. of bromine: Preparation of diperbromide of the pyrone.—A solution of bromine (0·2 c.c.) in chloroform (10 c.c.) was added to the solution of 2-methyl-3-phenyl-1 : 4-α-naphthapyrone (1 gm.) in chloroform (30 c.c.). On keeping the mixture for 24 hours the product crystallised out in white needles, m.p. 160° C. (Found: Br 35·7; $C_{20}H_{14}O_2B_{r_2}$ requires Br, 35·9 per cent.)

Action of sulphur dioxide solution on the diperbromide of 2-methyl-3-phenyl-1 : 4-α-naphthapyrone.—The diperbromide of the pyrone (0·2 gm.) was kept in SO_2 solution (50 c.c.) for 24 hours, the product was then washed and crystallised from chloroform in white needles, m.p. 210–11° and was 2-methyl-3-phenyl-1 : 4-α-naphthapyrone.

Action of glacial acetic acid on the diperbromide of 2-methyl-3-phenyl-1 : 4-α-naphthapyrone.—The diperbromide of the pyrone (0·2 gm.) was heated with glacial acetic acid (10 c.c.) on water-bath under reflux for three hours and the solution was then poured in water. The solid was filtered and crystallised through chloroform in white needles, m.p. 160° C. undepressed by the diperbromide of 2-methyl-3-phenyl-1 : 4-α-naphthapyrone.

Summary

The condensation of α-naphthol and phenyl acetyl chloride gave mainly 2-phenyl acetyl-1-naphthol and 4-phenyl acetyl-1-naphthol in small quantity. The former was brominated, nitrated, reduced, and acetylated by the Kostanecki method to give the pyrone. An attempt to prepare 4-phenylacetyl-1-naphthol the latter by dimethylation of 1-methoxy-4-phenylacetyl-naphthalene did not meet with success.

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FRIEDEL-CRAFTS REACTION

Part IX. The Action of Propionic and Butyric Anhydrides on Orcinol and Further Evidence of γ-Substitution in Resorcinol Derivatives

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As a result of the action of acetyl chloride and acetic anhydride on orcinol in presence of anhydrous aluminium chloride, it was observed by Desai and Vakil[1] that whereas the former gave a mixture of γ- and β-orcacetophenones the latter gave exclusively β-orcacetophenone. We have now found that propionic anhydride reacts with orcinol giving mainly 2-propionyl-5-methyl resorcinol (γ-orcpropiophenone) and a small quantity of 4-propionyl-5-methyl resorcinol (β-orcpropiophenone). Further, we have observed that butyric anhydride gives exclusively 2-butyryl-5-methyl resorcinol (γ-orcbutyrophenone). Thus this is a very convenient method of systhesising these inaccessible compounds, which have been characterised by their *p*-nitrophenylhydrazones.

As 2-propionyl-5-methyl-and 2-butyryl-5-methyl-resorcinols are unknown, we have studied their simple derivatives. They can be easily reduced to 2-propyl-5-methyl,-and 2-butyl-5-methyl-resorcinols. Further action of the anhydrides give the diacyl derivatives which lose the acyl group in the 4-position on keeping them in contact with concentrated sulphuric acid. An attempt to condense them with ethylaceto-acetate in presence of sulphuric acid gave 5-hydroxy-4:7-dimethyl coumarin with the removal of the propionyl and butyryl groups. The opening up of the lactone ring of this coumarin in presence of dimethyl sulphate gave the trans-2:6-dimethoxy-4-methyl-β-methylcinnamic acid which was unaffected by heat and light and gave 5-methoxy-4:7-dimethyl-coumarin by leaving in contact with concentrated sulphuric acid. Similarly the alkaline hydrolysis of 5-hydroxy-6-acetyl-4:7-dimethyl-coumarin gave the trans-2:6-dihydroxy-3-acetyl-4-methyl-β-methyl cinnamic acid as it was unaffected by heat and light, and underwent ring closure in presence of concentrated sulphuric acid giving the original coumarin. The monobromo derivative of the coumarin gave, on mild hydrolysis by sodium carbonate solution, 4-hydroxy-3:6-dimethyl coumarone, and 4-hydroxy-3: 6-dimethyl-coumarone-2-carboxylic acid.

EXPERIMENTAL

Action of propionic anhydride on orcinol and formation of 2-propionyl-5-methyl resorcinol (γ-orcpropiophenone).

Propionic anhydride (13·0 g.) was slowly added to the solution of anhydrous orcinol (12·4 g.) and anhydrous aluminium chloride (26·7 g.) in dry nitrobenzene (150 c.c.). The contents were heated for one hour on the water-bath after keeping the mixture at the room temperature overnight. After decomposing the mixture with ice-cold hydrochloric acid, nitrobenzene was removed in steam. The solid that separated out on cooling crystallised from dilute acetic acid in pale yellow needles m.p. 132-133°. Its alcoholic solution gave greenish-black coloration with ferric chloride (yield, 40%). (Found: C, 66·5, H, 6·8. $C_{10}H_{12}O_3$ requires C, 66·7; H, 6·7%.)

The acetic acid mother-liquor, on concentration gave a small quantity of a solid, the alcoholic solution of which gave reddish-brown coloration with ferric chloride, and was identified as 4-propionyl-5-methyl-resorcinol by the mixed m.p. with an authentic specimen (yield, 5%).

The p-*nitrophenyl-hydrazone* of γ-orcpropiophenone crystallised from alcohol in reddish micro needles m.p. 210°. (Found: N, 13·2. $C_{16}H_{17}N_3O_4$ requires N, 13·3%.)

2-Propyl-5-methyl resorcinol was obtained by reducing the above ketone (1 gm.) with amalgamated zinc (5 g) and dilute hydrochloric acid (20 c.c.). The solid crystallised from petrol (60–80 bp) in colourless needles m.p. 105°. (yield, 70%). (Found: C, 72·3; H, 8·7. $C_{10}H_{14}O_3$ requires C, 72·5; H, 8·5%).

2:4-*Dipropionyl-5-methyl-resorcinol* was obtained by condensing propionic anhydride (1·5 g.) with γ-orcpropiophenone (2 g.) in presence of aluminium chloride (3·5 g) in nitrobenzene (30 c.c.) The substance crystallised from dilute acetic acid in colourless, long needles m.p. 85–86°. Its alcoholic solution gave deep-violet coloration with ferric chloride (Found: C, 65·8; H, 6·7 $C_{13}H_{16}O_4$ requires C, 66·1; H, 6·8%.)

γ-orcbutyrophenone was obtained by the usual method using orcinol (12-4 g.), aluminium chloride (26·7 g.), and butyric anhydride (15·8 g.). The solid isolated as usual crystallised from dilute acetic acid in pale-yellow needles m.p. 120–121°. Its alcoholic solution gave greenish-black coloration with ferric chloride (yield, 40%). There was no trace of any isomeric compound. (Found: C, 68·1; H, 7·3. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·2%.)

The p-*nitrophenyl-hydrazone* crystallised from alcohol in reddish micro-needles m.p. 180°. (Found: N, 12·5; $C_{17}H_{19}N_3O_4$ requires N, 12·8%.)

2-*Butyl*-5-*methyl-resorcinol* obtained by the reduction of the above ketone crystallised from petrol (60–80 b.p.) in tiny needles m.p. 104° (yield, 70%). (Found: C, 73·1; H, 9·0. $C_{11}H_{16}O_2$ requires C, 73·2; H, 8·9%.)

2 : 4-*Dibutyryl*-5-methyl resorcinol obtained from the above ketone and butyric anhydride crystallised from dilute acetic acid in tiny needles m.p. 67°. Its alcoholic solution gave bluish-red coloration with ferric chloride. (Found: C, 67·9; H, 7·8. $C_{15}H_{20}O_4$ requires C, 68·2; H, 7·6%.)

Condensation of γ-orcpropiophenone and γ-orcbutyrophenone with Ethyl-acetoacetate and formation of 5-*hydroxy*-4 : 7-*dimethyl coumarin.*

A solution of either of the above ketones (2 g.) ethyl acetoacetate (1·3 g.) in concentrated sulphuric acid (15 c.c.) was left overnight. The coumarin crystallised from alcohol in needles m.p. 248–250, and was identified as 5-hydroxy-4 : 7-dimethyl coumarin by comparison with an authentic specimen.

Methylation and Hydrolysis of the above coumarin to 4-*methyl*-2 : 6-*dimethoxy-β-methyl-cinnamic acid.*

The mixture of the coumarin (2 g.) sodium hydroxide (20% 25 c.c.) and, dimethyl sulphate (10 c.c.) was heated on water-bath for one hour. Further quantity of dimethyl sulphate (5 c.c.) and sodium hydroxide (10 c.c.) was added, and refluxing was continued for another one hour and half. The cooled alkaline solution was acidified, extracted with ether and the recovered solid purified through sodium bicarbonate solution. It crystallised from dilute alcohol in lustrous lemon-yellow needles m.p. 205°. (Found: C, 65·9; H, 6·7. $C_{13}H_{16}O_4$ requires C, 66·1; H, 6·8%.)

Conversion of the dimethoxy acid to 5-*methoxy*-4 : 7-*dimethyl coumarin.*

A solution of the acid (0·5 g.) in concentrated sulphuric acid (10 c.c.) was allowed to stand for 48 hours, and worked up as usual. The solid crystallised from alcohol in needles m.p. 146°, and proved to be 5-methoxy-4 : 7-dimethyl coumarin by comparison with an authentic specimen.

3-*Bromo*-5-*hydroxy*-4 : 7-*dimethyl coumarin* was obtained by adding the solution of bromine (1 c.c.) in glacial acetic acid (5 c.c.) to the solution of coumarin (2 g.) in glacial acetic acid (20 c.c.) and crystallised from glacial acid in yellowish needles m.p. 217°. (Found: Br., 29·5. $C_{11}H_9O_3Br$, requires Br., 29·7%.)

Hydrolysis of the above bromo-compound with 5 per cent. sodium carbonate solution and isolation of 3:6-dimethyl 4-hydroxy coumarilic acid and 3:6-dimethyl-4-hydroxy-coumarone.

A solution of the bromo-coumarin (2 g.) in 5 per cent. sodium carbonate solution (40 c.c.) was heated on sand-bath under reflux for two hours. The solid that separated out on cooling was filtered, and the filtrate, on acidification gave an acid, which after purification through sodium bicarbonate solution slightly decomposed at 250°, but did not melt upto 320°. (Found: C, 63·8; H, 5·0. $C_{11}H_{10}O_4$ requires C, 64·1; H, 4·9%.)

The solid which was insoluble in sodium carbonate, but soluble in sodium hydroxide crystallised from alcohol in small needles m.p. 320°. (Found: C, 74·0; H, 6·3. $C_{10}H_{10}O_2$ requires C, 74·1; H, 6·2%.)

Hydrolysis of 5-hydroxy-6-acetyl-4:7-dimethyl coumarin and Formation of 2:6-dihydroxy-3-acetyl-4-methyl-β-methyl cinnamic acid.

The solution of the coumarin (2 g.) prepared according to Desai and Ekhlas[2] in 20% sodium hydroxide (50 c.c.) was heated on a water-bath for one hour. The cooled solution was acidified with concentrated hydrochloric acid. The resulting acid after purification through sodium bicarbonate solution crystallised from alcohol in tiny needles m.p. 244–246°. Its alcoholic solution gave reddish coloration with ferric chloride. The acid was unaffected by heat and light, and reverted to the original coumarin on treatment with concentrated sulphuric acid in the cold. (Found: C, 62·1; H, 5·8. $C_{13}H_{14}O_5$ requires C, 62·4; H, 5·6%.)

We take this opportunity of expressing our thanks to Rev. Father A. M. Coyne, S. J., for his kind interest in this work.

Summary

The study of the action of propionic and butyric anhydrides in presence of anhydrous aluminium chloride on orcinol shows that γ-substitution takes place almost exclusively. Therefore, this provides a convenient method for the synthesis of hitherto unknown γ-orc-propiophenone and γ-orc-butyrophenone. Some of their interesting derivatives have been prepared. A study has been made of some deivatives of 5-hydroxy-4:7-dimethyl-coumarin.

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STUDIES ON THE NATURE OF THE RACEMIC MODIFICATION OF OPTICALLY ACTIVE COMPOUNDS

Part V. Roozeboom Solubility Composition Isotherms for Mixtures of Active and Inactive Camphoric Acids in Water at 25° C., 45° C., and 100° C.

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The present work is in continuation of Part III in this series.[1] The solubility-composition isotherms for mixtures of active and inactive camphoric acids in water at 25° C., 45° C. and at the boiling points of the solutions have been determined with a view to ascertain the variation of the solubility isotherms with temperature, and if possible, to find out the temperature of transition of the rasemic compound into the racemic mixture.

Roozeboom[2] and also Bruni[3] have theoretically discussed, from the phase rule standpoint, the solubility relations existing between optical isomerides and their racemic forms (mixtures, compounds, or solid solutions). The solubility composition isotherm for a simple mixture of *d*- and *l*-isomers without the formation of a racemic compound would give a curve consisting of two parts having a maximum of solubility at the isothermal invariant point for the *d*- and *l*-forms. In the case of a racemic compound, the curve would consist of three parts with two invariant points, one for the *d*-*dl*-system, the other for the *l*-*dl*-system.

It may be pointed out that the Bruni-Roozeboom solubility isotherms of mixtures of optically active and inactive forms in a given solvent at different temperatures would form a family of curves in which the isothermal invariant points would all lie on a smooth curve (MON) symmetrical about the *dl*-axis and cutting it at some point O (Figs. 1 and 2). The temperature at which the solubility of the *dl*-form corresponds to this point of intersection (O) gives the transition point. At all temperatures where the solubility of the inactive form lies on the concave side of the curve (MON) connecting the invariant points, the racemic form exists as a *dl*-compound; at all temperatures on the convex side, as a *dl*-mixture,

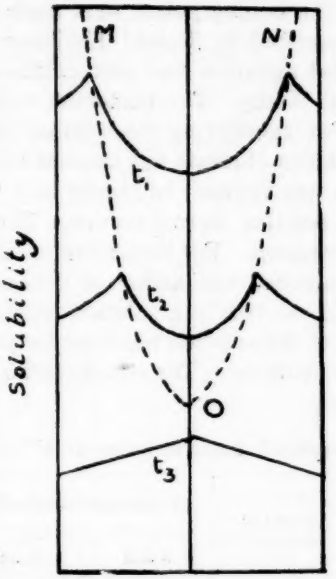

FIG. 1

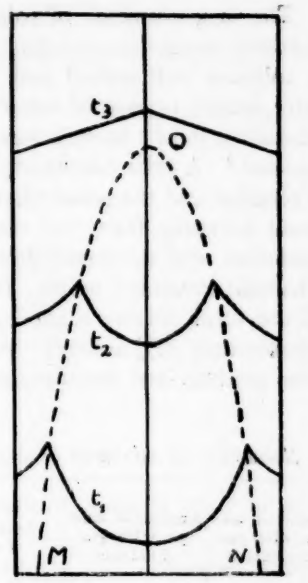

FIG. 2

Camphoric acids[1] and camphor-β-sulphonic acids[4] are the only cases, in which as far as we are aware, Roozeboom solubility-composition isotherms giving the solubility relations which exist between the optical enantiomorphs and the racemic forms have been investigated, and the exact shape and slopes of the curves determined. The inactive acids in both cases were shown to be *dl*-compounds, a result in complete agreement with our previous studies by the Roozeboom freezing point method.[5] In the present paper we adduce further data in support of the racemic camphoric acid being a *dl*-compound. It is also shown that the transition temperature (from racemic compound to racemic mixture) of camphoric acid-water system lies considerably above 100° C.

EXPERIMENTAL

The *d*-, *l*- and *dl*-camphoric acids were prepared and purified by the methods described by Singh and Mahanti.[6] The measurements of solubility at 25° C. and 45° C. were made in the apparatus described in Part III.

The measurements of solubility at the boiling points were made in an apparatus similar in principle to one described by Seidel.[7] Ebullition kept the solution well stirred and mechanical agitation was also employed to ensure proper release of supersaturation, if any. The maximum temperature during steady boiling was noted. For transferring the solution suction was used.[8] A tube containing fused calcium chloride was inserted between the receiver and the point where suction was applied, to absorb any water vapour escaping from the transferred solution during suction. The acid in solution was estimated directly by titration. For determination of the isothermal invariant points, 10 c.c. of alcohol was added to the receiver and the total volume made upto 100 c.c. so that the solution contained approximately 10% alcohol. A portion of the solution was used for polarimetric analysis and another portion for titration. The specific rotation of

TABLE I

Solubility of mixtures of d- *and* dl-*camphoric acids in water at* 45° *C.*

Amount of acid (gm.)/100 gm. of solution	Amount of acid (gm.)/100 gm. of solvent	Amount of *d*-acid	Amount of *dl*-acid	Percentage composition	
				d-acid	*dl*-acid
1·127	1·140	1·140	..	100·0	0·0
1·151	1·164	1·102	·062	94·6	5·4
1·163	1·177	1·101	·076	93·5	6·5
0·885	0·893	0·804	·089	90·1	9·9
0·750	0·756	0·668	·088	88·4	11·6
0·620	0·624	0·533	·091	85·5	14·5
0·494	0·497	0·400	·097	80·6	19·4
0·386	0·388	0·267	·121	68·9	31·1
0·339	0·340	0·134	·206	39·2	60·8
0·317	0·318	..	·318	0·0	100·0

TABLE II

Solubility of mixtures l- *and* dl-*camphoric acids in water at* 45° *C.*

Amount of acid (gm.)/100 gm. of solution	Amount of acid (gm.)/100 gm. of solvent	Amount of *l*-acid	Amount of *dl*-acid	Percentage composition	
				l-acid	*dl*-acid
1·132	1·145	1·145	..	100·0	0·0
1·148	1·161	1·111	0·050	95·7	4·3
1·165	1·179	1·101	0·078	93·4	6·6
0·730	0·735	0·649	0·086	88·2	11·8
0·576	0·579	0·486	0·093	83·9	16·1
0·432	0·434	0·323	0·111	74·5	25·5
0·343	0·344	0·162	0·182	46·9	53·1
0·317	0·318	..	0·318	0·0	100·0

TABLE III

Solubility of mixtures of d- *and* dl-*camphoric acids in water at* 25° *C.*

Amount of acid (gm.)/100 gm. of solution	Amount of acid (gm.)/100 gm. of solvent	Amount of *d*-acid	Amount of *dl*-acid	Percentage composition	
				d-acid	*dl*-acid
0·725	0·730	0·730	..	100·0	0·0
0·725	0·730	0·699	0·031	95·7	4·3
0·727	0·732	0·692	0·040	94·5	5·5
0·535	0·538	0·495	0·043	92·0	8·0
0·410	0·412	0·371	0·041	90·0	10·0
0·314	0·315	0·247	0·068	78·5	21·5
0·235	0·236	0·123	0·113	52·3	47·7
0·228	0·229	0·049	0·180	21·5	78·5
0·226	0·227	..	0·227	0·0	100·0

TABLE IV

Solubility of mixtures of l- *and* dl-*camphoric acids in water at* 25° *C.*

Amount of acid (gm.)/100 gm. of solution	Amount of acid (gm.)/100 gm. of solvent	Amount of *l*-acid	Amount of *dl*-acid	Percentage composition	
				l-acid	*dl*-acid
0·718	0·723	0·723	..	100·0	0·0
0·726	0·731	0·700	0·031	95·7	4·3
0·727	0·732	0·692	0·040	94·5	5·5
0·363	0·364	0·313	0·051	86·0	14·0
0·251	0·252	0·156	0·096	62·2	37·8
0·229	0·230	0·078	0·152	33·9	66·1
0·226	0·227	..	0·227	0·0	100·0

TABLE V

Solubility of camphoric acids at boiling point of water

Solubility of *dl*-camphoric acid in water (100·2° C.) = 2·412 gm./100 gm. solution

Solubility of *d*-camphoric acid in water (100·4° C.) = 8·325 gm./100 gm. solution

Solubility of *l*-camphoric acid in water (100·4° C.) = 8·429 gm./100 gm. solution

Solubility at the invariant point (100·4° C.) (*d*+*dl*-) = 8·954 gm./100 gm. solution

Solubility at the invariant point (100·4° C.) (*l*+*dl*-) = 9·015 gm./100 gm. solution

Specific rotation in 10% alcohol $[\alpha]^{35°}_{5461} = \pm 55°$

The percentage of *d*-acid at invariant point = 87·5

The percentage of *l*-acid at invariant point = 88·1

TABLE VI

The percentage composition of camphoric acid at the isothermal invariant point at different temperatures

Temperature (°C.)	Iso. Inv. point of *d-dl*-system	Iso. Inv. point of *l-dl*-system
25	94·5 *d*-acid	94·5 *l*-acid
35	94·1 ,,	94·0 ,,
45	93·3 ,,	93·4 ,,
100	87·5 ,,	88·1 ,,

camphoric acid in " 10% " alcohol, at approximately the same concentration, was determined to calculate the amount of the active form corresponding to the rotation measured for the invariant points.

DISCUSSION

The results given in Tables I, II, III and IV are plotted in Fig. 3. The total solubility in 100 gm. of water is plotted against the percentage composition of the mixtures. The *l-dl*-portions of the graphs are drawn as mirror images of the *d-dl*-portions. The points corresponding to actual determination of the *l-dl*-system are found to fit on these curves. The solubility composition isotherm for 35° C., described in Part III, is also included for the sake of comparison.

It is found from the graphs that the curves for 25°, 35° and 45° C. are quite similar. In every case there are two invariant points and three curves. showing that the racemic form exists as a compound at all these temperatures The presence of the invariant points at the temperatures of boiling of the solution, indicates the existence of the racemic camphoric acid as a *dl*-compound at those temperatures also.

A study of the isothermal invariant points for the camphoric acid-water system at different temperatures (Table VI) shows that there is a slow shifting of these points nearer to the *dl*-axis with increasing temperature (thus corresponding to Fig. 2 discussed above). This points to the decreasing stability of the *dl*-camphoric acid as a compound as the temperature rises. The shift is not considerable, even over a temperature range of 75° C. Since at the transition point the percentage of the *dl*-compound is zero, we may expect that this temperature is high indeed.

A correlation is possible between the solubility curves and the melting point curves. The percentage composition at the eutectic points as deter-

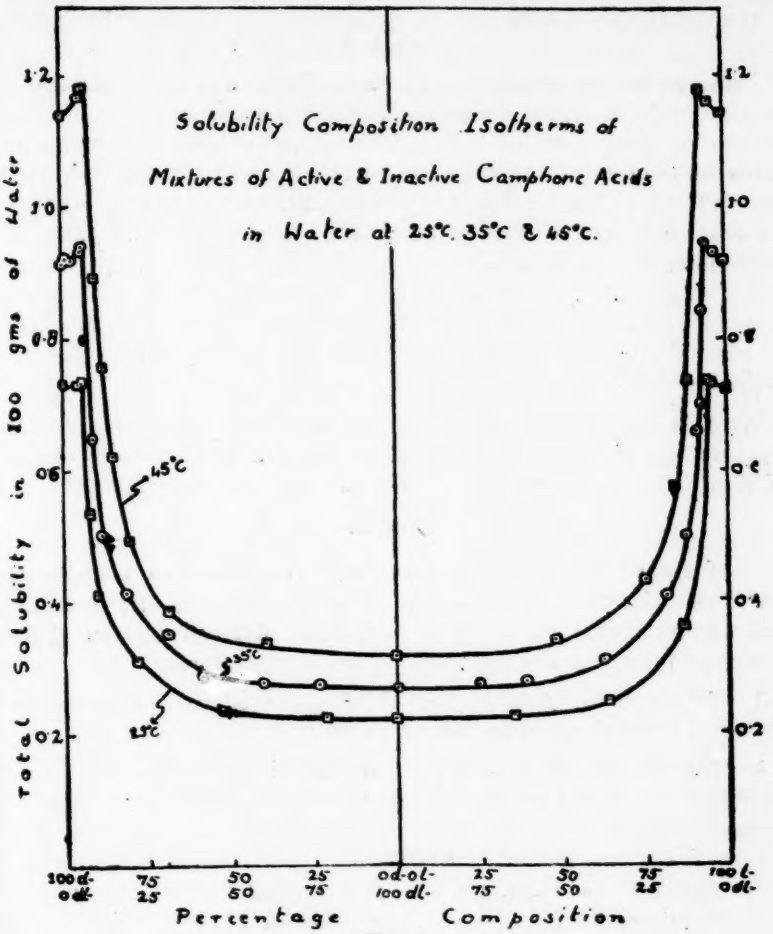

FIG. 3

mined by Singh and Perti was 80 *d*-: 20 *dl*-. This is quite in keeping with our present results which give approximately 88 *d*-: 12 *dl*- at 100° C. The transition temperature thus appears to be much higher than even the melting points. The evidence for the existence of racemic compounds in the liquid state is rather conflicting and it is, therefore, hazardous to make any guess about the temperature of transition of inactive camphoric acid from the *dl*-compound to the *dl*-mixture. An upper temperature limit for the measurement of these solubility isotherms in the case of camphoric acids is set as the acid changes into the anhydride above its melting point.

It is interesting to note here the latent heats of fusion of the three camphoric acids. According to Ross and Somerville,[9] the latent heats are 4,835 calories for the *d*- and *l*- forms and 13,840 calories for the *dl*- form. The great difference in the latent heats of the active and inactive forms points to the great stability of the *dl*- compound even at the melting point. Making allowance for the variation of latent heats for different melting points (188–89° C. for the active forms and 202–03° C. for the racemic) the extra heat consumed is likely to have been utilised for the breaking up of the *dl*- molecules into *d*- and *l*- forms. This dissociation being thus endothermic, we should expect by Le Chatelier's principle that rise in temperature will favour dissociation. The transition temperature may thus be expected to be beyond the temperatures of fusion, a result entirely in accordance with our present conclusion.

We wish to thank the University of Allahabad, where this work was carried out, for the grant of the Empress Victoria Readership to one of us (B.K.K.N.) which enabled him to take part in these investigations.

Summary

1. The solubility composition isotherms of camphoric acids in water at 25° C., 45° C. and at the boiling points of the solutions have been determined. In each case three curves have been obtained showing that the racemic form is a true *dl*-compound at these temperatures.

2. The results obtained by the solubility method are in agreement with those already obtained from melting point data.

3. The temperature of transition of racemic camphoric acid from the compound into the mixture of optically active and opposite forms has been discussed.

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THERMO-OPTIC BEHAVIOUR OF SOLIDS

IV. Zinc-Blende

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1. Introduction

Zinc-blende is a cubic crystal with a high index of refraction of about 2.5. It exhibits strong absorption for wave-lengths below 4000 Å.U. Over the whole range of the visible spectrum, its refractive index has been determined for a number of wavelengths and also over a large range of temperatures (Maria Mell, 1923). These data show that not only is the dispersion of zinc-blende very large, but that the refractive index also varies appreciably with temperature. As is the case with diamond, the refractive index increases with rise of temperature, but the increase is nearly 5 times more with zinc-blende than with diamond. Thus, on heating from 0° to 400° C. the refractive index of diamond increases by 0·01 for 4358 Å.U. (Ramachandran, 1947*a*) while for zinc-blende, the increase is 0·045. As shown in the earlier parts of these series, a positive value for dn/dt must be attributed to a large shift in the position of the dispersion frequencies, the positive contribution of which to dn/dt must overbalance the negative contribution due to thermal expansion. For diamond, the coefficient of cubical expansion is about 3×10^{-6}, but for zinc-blende it is larger, being nearly 20×10^{-6}. Consequently, the proportionate rate of change of the dispersion frequencies $d(\log \nu)/dt$ (which is equal to $-\chi$, following the notation of the earlier papers) must be numerically much larger than for diamond. It has been calculated to be nearly 10 times as large as for diamond, and of the same order as for fluorspar. It is also found that, just as with diamond, the dispersion frequency alters less at lower temperatures that at higher ones.

2. Calculation of the Thermal Change of Refractive Index for Different Wave-lengths

Mell (*loc. cit.*) has shown that her data for the refractive indices at 0° C. can be fitted by the formula

$$n^2 = 3.0221 + 2.0998\ \lambda^2/\{\lambda^2 - (0.2532)^2\} \qquad (1)$$

where λ is expressed in microns. Studies of Coblentz (1906, 1908) show that there are no characteristic infra-red frequencies on the shorter wavelength side of 15μ, so that one may neglect the contribution to dn/dt due to the alteration of the infra-red frequency and use Eq. (1) for calculating dn/dt.

Mell's measurements include two sets of data for refractive indices at various wave-lengths between 4000 Å.U. and 7500 Å.U., one at temperatures close to 0° C. and the other at temperatures near about 205° C. From these, the change in refractive index from 0° to 205°C. was calculated for each wave-length. If one denotes this by Δn, then writing (1) in the form

$$n^2 = C + a\lambda_1^2\lambda^2/(\lambda^2 - \lambda_1^2), \tag{2}$$

one obtains from the general theory given in Part I (Ramachandran, 1947*a*)

$$\Delta n = \frac{\Delta C}{2n} + \frac{\Delta \rho}{\rho} \cdot \frac{(n^2 - C)}{2n} + \frac{a\lambda_1^2}{n} \cdot \frac{\lambda^4}{(\lambda^2 - \lambda_1^2)^2} \cdot \frac{\Delta \lambda_1}{\lambda_1}, \tag{3}$$

where ρ is the density of the substance, and Δ represents the difference between the values of the respective quantities at 205° and 0° C. In the right hand side of (3), $\Delta\rho/\rho$ can be claculated, if one knows the thermal expansion coefficient. Fizeau has shown (Liebisch, 1891) that the coefficient of linear expansion α_t at $t°$ C. is given by

$$\alpha_t = 6{\cdot}70 \times 10^{-6} + 12{\cdot}8 \times 10^{-9}(t - 40). \tag{4}$$

From this, $\Delta\rho/\rho$ comes out to be $4{\cdot}614 \times 10^{-3}$. There are thus only two quantities to be determined, namely ΔC and $(\Delta\lambda_1/\lambda_1)$ which have been calculated from the experimental data to have the values

$$C = -\,8{\cdot}60 \times 10^{-3}; \quad \Delta\lambda_1/\lambda_1 = 14{\cdot}2 \times 10^{-3}. \tag{5}$$

In Fig. 1 the continuous curve represents the variation of Δn with wave-length according to theory using these values, while the circles represent the experimental data deduced from Mell's measurements. It will be seen that theory and experiment agree fairly well, thus verifying the correctness of Eq. (3).

3. Explanation of the Course of the Refractive Index-Temperature Curve

We have seen how it is possible to explain the variation with wave-length of Δn from 0° to 200° C. by means of Eq. (3). In this section it will be shown that the same formula enables one to calculate the refractive index-temperature curves for different wave-lengths. Mell (*loc. cit.*) has measured the refractive indices at various temperatures between − 80° and + 700° C. for four wavelengths, namely 0·436, 0·546, 0·578 and 0·619 μ. From these data, the refractive indices at temperatures − 80°, 0°, 200°, 400°,

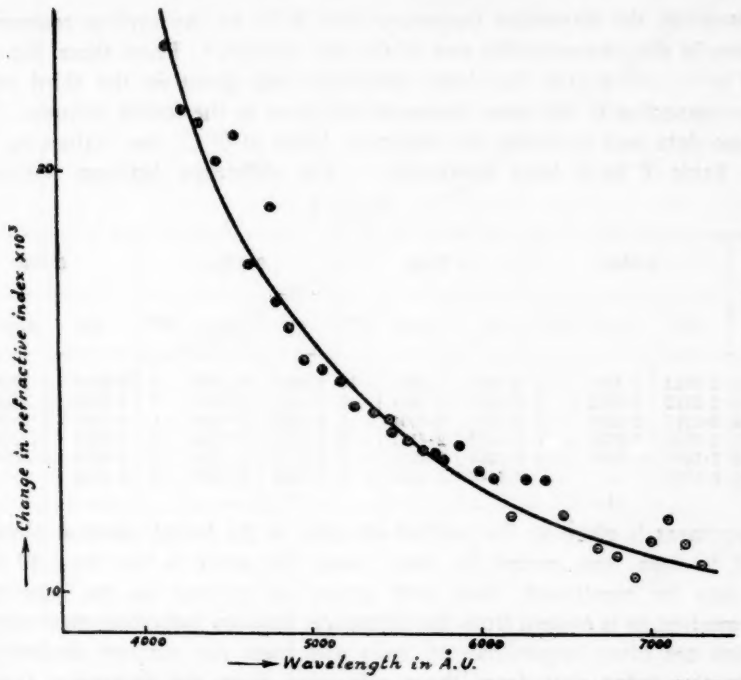

FIG. 1. Figure showing how the change in refractive index on heating from 0° to 205°C. varies for different wavelengths. The continuous curve is from theory while the points represent the experimental data.

600° and 700° C. have been calculated by interpolation and are given as n_{exp} in Table I. To explain these, we shall follow the procedure adopted with fused silica in Part II (Ramachandran, 1947*b*). It is assumed that ΔC in (3) arises from a density change only, so that the first two terms in the right hand side of (3) both vary as $\Delta\rho/\rho$, which can be calculated from the coefficient of expansion. Although the coefficient of linear expansion has not been determined at the higher temperatures, it is assumed that Fizeau's expression for α_t holds good at these temperatures also, and $\Delta\rho/\rho$ is calculated from it. Unlike with fused quartz, one has no data regarding the variation of the lattice frequency of zinc-blende over these temperatures. This deficiency can be overcome and formula (3) verified as follows. We shall show that, by assuming a certain course of variation for the dispersion frequency, the courses of the refractive index-temperature curves *for all the four wavelengths* can be correctly predicted from theory. This course is given in the second column of Table II, which contains the percentage

change of the dispersion frequency from 0° C. to the various temperatures given in the corresponding row of the first column.* From these, the values of $\chi = -d(\log \nu)/dt$ has been calculated and given in the third column corresponding to the mean temperatures given in the fourth column. Using these data and assuming the refractive index at 0° C., the values n_{th} given in Table I have been computed. The difference between theory and

TABLE I

Temperature °C	0·436μ			0·546μ			0·578μ			0·619μ		
	n_{th}	n_{exp}	diff.	n_{th}	n_{exp}	diff.	n_{th}	n_{exp}	diff.	n_{th}	n_{exp}	diff.
−80	2·4814	2·4803	+11	2·3821	2·3837	−16	2·3667	2·3673	−6	2·3510	2·3506	+4
0	2·4882	2·4882	0	2·3867	2·3867	0	2·3709	2·3709	0	2·3549	2·3549	0
200	2·5087	2·5089	− 2	2·4005	2·4004	+ 1	2·3837	2·3838	−1	2·3667	2·3665	+2
400	2·5339	2·5331	+ 8	2·4173	2·4177	− 4	2·3993	2·3990	+3	2·3811	2·3812	−1
600	2·5630	2·5616	+14	2·4365	2·4363	+ 2	2·4170	2·4175	−5	2·3974	2·3980	−6
700	2·5762	..	..	2·4449	2·4448	+ 1	2·4247	2·4252	−5	2·4045	..	..

experiment is given as the number of units in the fourth decimal place. It will be seen that, except for three cases, the error is less than 10 units. It may be mentioned that such errors are present in the experiments themselves, as is evident from the differences between individual measurements which are often larger than 10 units and from the random deviations of refractive index data from those calculated from the dispersion formula, which are sometimes as large as 11 units (see pp. 250 and 257 in Mell's paper quoted). The agreement between theory and experiment is appreciated better when one looks at Fig. 2, where the continuous curves are from theory and the circles represent the measurements of Mell. As already remarked the curve is made to pass through the experimental point at 0° C.

TABLE II

Temperature °C.	Percentage change of frequency	$\chi \times 10^6$ at t° C.	
− 80	+0·45	56	− 40
0	0·0	70	100
200	−1·39	87	300
400	−3·13	103	500
600	−5·18	99	650
700	−6·17		

* These were calculated actually from the experimental data backwards using Eq. (3). It was found that $\Delta\lambda_1/\lambda_1$ calculated from the four wavelengths were very nearly the same and the mean is given in Table II.

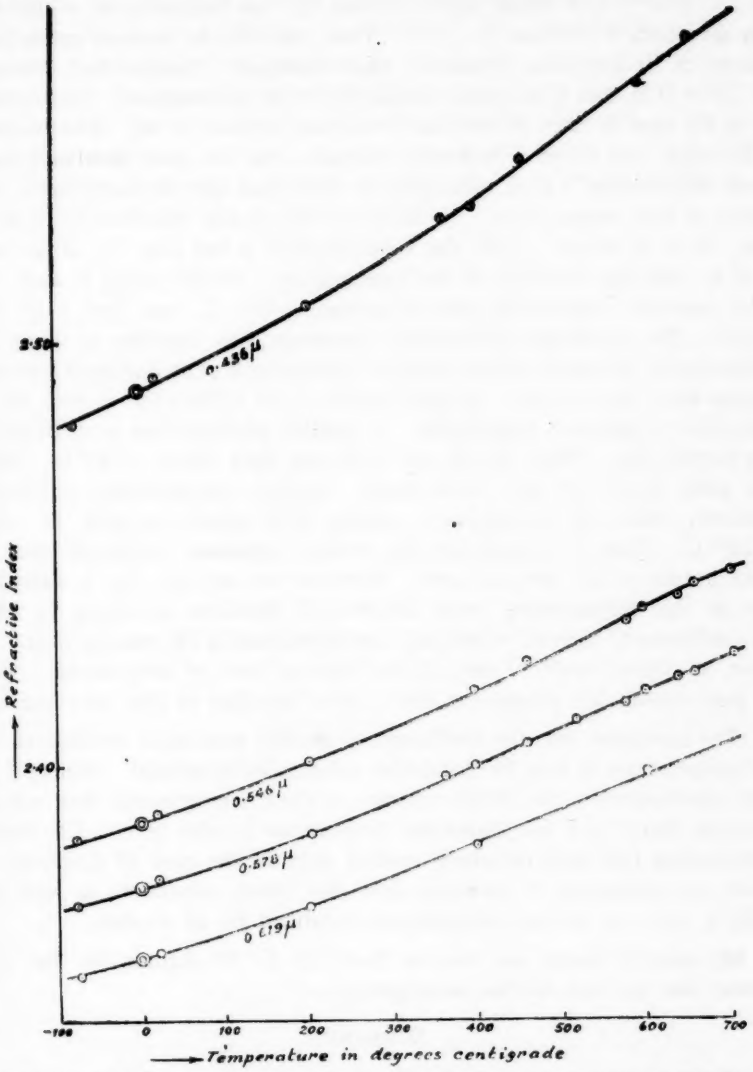

FIG. 2. Variation of refractive index with temperature from—100° to 700° C. The figures represent the wavelengths in microns. The continuous curve from theory has been made to pass through the experimental point at 0° C.

One notes that χ is fairly large, being about 70×10^{-6} at 100° C. This is much larger than the mean χ for the ultra-violet frequencies of fluorspar,

viz., 35×10^{-6}, and nearly equal to that for the frequency at λ 1115 Å.U. For diamond, χ is about 8×10^{-6}. Thus, zinc-blende shows a much larger change of its dispersion frequency than diamond. Another fact evidenced by Table II is that χ increases numerically with temperature. This is found to be the case in three of the four substances studied so far. The exception is fluorspar, for which χ is nearly constant; but we have data only above room temperature. It is interesting to note that the tendency for χ is to vanish at low temperatures. In diamond, this is seen particularly to be the case. Even at about $-150°$ the value of dn/dt is less than 5% of the value at 0° C. and the tendency of the temperature $-(dn/dt)$ curve is such that dn/dt becomes practically zero at about $-180°$ C. (see Part I of these series). The coefficient of thermal expansion also vanishes at these low temperatures, so that it follows that the contribution to dn/dt due to frequency change must also vanish. In other words, χ or $d(\log \nu)/dt$ is zero for the ultra-violet dispersion frequencies. A similar phenomenon is exhibited by zinc-blende also. Here, we do not have any data below $-80°$ C. But if one plots dn/dt for any wave-length against temperature, a curve is obtained, which on extrapolation, makes dn/dt equal to zero at about $-250°$ C. Fizeau's formula for the thermal expansion coefficient does not make it zero at the absolute zero. However we can say that it should be zero at this temperature, from Gruiniesen's theorem according to which the coefficient of thermal expansion is proportional to the specific heat. The latter, of course, tends to zero at the absolute zero of temperature. Thus, we may reasonably conjecture that χ also vanishes at the absolute zero.

The statement that the coefficient of thermal expansion vanishes at very low temperatures is true for crystalline substances in general. Hence, if one finds experimentally that dn/dt vanishes at these temperatures then one can conclude that χ for the dispersion frequencies is also zero. The former phenomenon has been definitely verified only in the case of diamond. It would be interesting to measure dn/dt for other substances as well and verify if this is a general phenomenon exhibited by all crystals.

My sincere thanks are due to Prof. Sir C. V. Raman for the kind interest that he took in this investigation.

Summary

The refractive index of zinc-blende increases appreciably on heating for all wavelengths in the visible region the increase being 0·0212 and 0.0107 respectively for wavelengths 4358 Å.U. and 7320 Å.U. on heating from 0° to 205° C. It is shown that by applying the general theory of Part I one can satisfactorily explain both the variation of dn/dt with

wavelength and the courses of the temperature—refractive index curves from $-80°$ to $700°$ C. for different wavelengths. The calculations show that the ultra-violet dispersion frequency at 2532 Å.U. alters appreciably with temperature, the proportional rate of change $\chi = -d(\log \nu)/dt$ being 70×10^{-6}. This is nearly ten times the corresponding rate for diamond. The rate of change becomes less and less on lowering the temperature. It is pointed out that, for diamond, χ actually vanishes at very low temperatures and this is also probably the case for zinc-blende.

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TEMPERATURE VARIATION OF THE REFRACTIVE INDICES OF QUARTZ

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1. Introduction

The variations of the refractive indices of quartz with temperature present some interesting features. At the shortest wave-length (about λ 2000) at which measurements are available, both the ordinary and extraordinary indices increase with rising temperature. On the other hand, in the visible spectrum, the temperature coefficients are negative and become numerically larger as the wave-length is increased. The temperature coefficients of the extraordinary and ordinary indices differ considerably throughout, much more so than the indices themselves.

In the present paper, a quantitative explanation of these features is offered on the basis of a theory recently put forward and applied with success to several isotropic solids by Mr. G. N. Ramachandran (1947). Ramachandran pictures the change in refractive indices due to an increase in temperature as arising from a superposition of the following effects:—

(A) a diminution due to the decreased number of oscillators per unit volume as the crystal expands.

(B) an increase, due to the shift towards longer wave-lengths of the characteristic ultra-violet absorptions.

In the particular case of vitreous silica, discussed in detail by Ramachandran, the thermal expansion, and therefore the effect (A) is nearly negligible, so that we have a steady increase of refractive index with rising temperature. On the other hand, in crystalline quartz, both effects have to be considered and effect (A) is greater than (B) for wave-lengths longer than λ 2100, thereby making the temperature coefficients negative.

2. The Dispersion Formulae of Quartz

Accurate measurements of the temperature coefficients extend over the region λ 2000 to λ 6500. In this region, the dispersion of both the indices is principally determined by an ultra-violet characteristic frequency, which

was first calculated by Rubens (1897) from the dispersion data to be in the neighbourhood of λ 1000. Subsequently, Lowry and Coode-Adams (1927–28) showed that the refractive dispersion as well as the dispersion of optical rotatory power, could be accurately explained by a term at λ 1127. Recently (1936) Tousey has shown experimentally that quartz exhibits two maxima of selective reflection at λ 1190 and λ 1060. The choice of λ 1127 which is nearly a mean of these two, is thus seen to be a happy one, and it explains the refractive indices with sufficient accuracy for our purpose. In addition, there are contributions to refraction from infra-red and remote ultra-violet terms. The contributions of the infra-red terms are very small in the region under consideration, so that variations due to a shift in the infra-red characteristic frequencies are negligible. The contributions from the remote ultra-violet arise from purely atomic transitions in silicon and oxygen. The characteristic frequencies, therefore, cannot be expected to change with temperature. Consequently, the purpose of investigating the temperature coefficients would be satisfied by dispersion formulæ which stress the importance of the term at λ 1127 and express the contributions by the other terms in as simple a manner as possible. Such formulæ have been obtained here as simplifications of formulæ originally proposed by Coode-Adams. They are,

$$n_\omega^2 = 1{\cdot}7239 + 0{\cdot}002682\ \nu^2 + \frac{49{\cdot}630}{78{\cdot}436 - \nu^2} - \frac{0{\cdot}0109}{\nu^2} \qquad (1)$$

$$n_e^2 = 1{\cdot}7210 + 0{\cdot}002761\ \nu^2 + \frac{51{\cdot}962}{78{\cdot}436 - \nu^2} - \frac{0{\cdot}0109}{\nu^2} \qquad (2)$$

$$\left(\nu = \frac{1}{\lambda_{\text{microns}}}\right)$$

The first two terms contain the contribution of the remote ultra-violet, the last term expresses the contribution of the infra-red and the third term the frequency at λ 1127. The agreement of these formulæ with the facts is set out below, in Table I.

TABLE I

Wavelength (microns)	n_ω (calculated)	n_ω (observed)	n_e (calculated)	n_e (observed)
0·20255	1·6453	1·6456	1·6580	1·6584
0·312279	1·5742	1·5743	1·5844	1·5845
0·467815	1·5510	1·5510	1·56035	1·56037
0·64385	1·5423	1·5423	1·5513	1·5513

This degree of agreement, though not as perfect as that to be expected of a regular dispersion formula, is sufficiently good for the present purpose.

3. Application

Formulæ (1) and (2) are of the form

$$n^2 = a + c\nu^2 + \frac{b}{\nu_0^2 - \nu^2} - \frac{e}{\nu^2}$$

$$= a + f(\rho, \nu_0), \tag{3}$$

where ρ is the density of the crystal. If t be the temperature,

$$2n\frac{dn}{dt} = \frac{da}{dt} + \frac{\partial f}{\partial \rho}\frac{d\rho}{dt} + \frac{\partial f}{\partial \nu_0}\frac{d\nu_0}{dt}. \tag{4}$$

In this form of dispersion formula, the oscillator strengths b, c and e are simply proportional to the density of the crystal, so that the dependance of f on ρ can be written as

$$f(\rho) = k\rho, \tag{5}$$

where k is a constant.

$$\therefore \quad \frac{\partial f}{\partial \rho}\frac{d\rho}{dt} = k\frac{d\rho}{dt} = -k\gamma_t\rho = -\gamma_t f$$

$$= -\gamma_t(n^2 - a), \tag{6}$$

where γ_t is the coefficient of cubical expansion at the temperature t. Also

$$\frac{\partial f}{\partial \nu_0}\frac{d\nu_0}{dt} = -\frac{2b\nu_0}{(\nu_0^2 - \nu^2)^2}\frac{d\nu_0}{dt}$$

Let us write, for convenience,

$$\frac{d(\log \nu_0)}{dt} = \frac{1}{\nu_0}\frac{d\nu_0}{dt} = \chi_t, \tag{7}$$

where χ_t itself can be a function of temperature. Substituting (6) and (7) in (4), we get

$$2n\frac{dn}{dt} = \frac{da}{dt} - \gamma_t(n^2 - a) - \frac{2b\nu_0^2}{(\nu_0^2 - \nu^2)^2}\chi_t$$

or

$$2n\frac{dn}{dt} = A + \frac{B\chi_t}{(\nu_0^2 - \nu^2)^2} \tag{8}$$

where

$$A = \frac{da}{dt}; \quad B = -2b\nu_0^2.$$

Applying these to the two indices, we get

$$2n_\omega\frac{dn_\omega}{dt} + \gamma_t(n_\omega^2 - a_\omega) = A_\omega + \frac{B_\omega\chi_t}{(\nu_0^2 - \nu^2)^2}$$

$$2n_e\frac{dn_e}{dt} + \gamma_t(n_e^2 - a_e) = A_e + \frac{B_e\chi_t}{(\nu_0^2 - \nu^2)^2}.$$

Thus, if the left-hand sides of both these equations are computed, and plotted against $\frac{1}{(\nu_0^2-\nu^2)^2}$, two straight lines should be obtained, whose slopes should give $B_\omega\chi_t$ and $B_e\chi_t$ and whose y-intercepts should give A_ω and A_e. This was actually done, using Micheli's experimental values of $\frac{dn_\omega}{dt}$ and $\frac{dn_e}{dt}$ (1902) reduced to vacuum, and at a mean temperature of 60° C. The graphs were both straight lines, thus verifying the theory, and Micheli's data were found to be well expressed by the following formulæ:

$$2n_\omega\frac{dn_\omega}{dt}+35\cdot6\times10^{-6}(n_\omega^2-1\cdot7239)=-36\cdot23\times10^{-6}+\frac{0\cdot227}{(78\cdot44-\nu^2)^2} \quad (9)$$

$$2n_e\frac{dn_e}{dt}+35\cdot6\times10^{-6}(n_e^2-1\cdot7210)=-40\cdot43\times10^{-6}+\frac{0\cdot238}{(78\cdot44-\gamma^2)^2} \quad (10)$$

The values of χ_t, computed from (9) and (10) are

$$\chi_t=-\frac{0\cdot227}{2\times49\cdot63\times78\cdot44}=-\underline{2\cdot92\times10^{-5}}$$

$$\chi_t=-\frac{0.238}{2\times51\cdot96\times78\cdot44}=-\underline{2\cdot92\times10^{-5}}$$

The values derived from the temperature-variations of the ordinary and extraordinary indices thus agree perfectly. The values of the temperature coefficients, calculated from (9) and (10) are compared with the experimental values in Table II and the graph (Fig. 1) shows theoretical curves of $\frac{dn}{dt}$ against λ with the experimental points marked side by side. No systematic error is seen. The value of χ_t is of the same order of magnitude as Ramachandran's value (-2.5×10^{-5}) for $d(\log\nu)/dt$ of the characteristic frequency at λ 1070 in vitreous silica.

TABLE II

Approx. wave-length (microns)	$\frac{dn_\omega}{dt}10^6$ (calculated)	$\frac{dn_\omega}{dt}10^6$ (observed)	$\frac{dn_e}{dt}10^6$ (calculated)	$\frac{dn_e}{dt}10^6$ (observed)
0·202	+1·95	+1·84	+1·28	+1·29
0·257	−2·81	−3·09	−3·67	−3·89
0·312	−4·54	−4·65	−5·50	−5·68
0·340	−5·02	−5·08	−6·0	−6·17
0·467	−6·08	−5·96	−7·14	−7·15
0·508	−6·26	−6·26	−7·29	−7·29
0·643	−6·56	−6·60	−7·64	−7·64

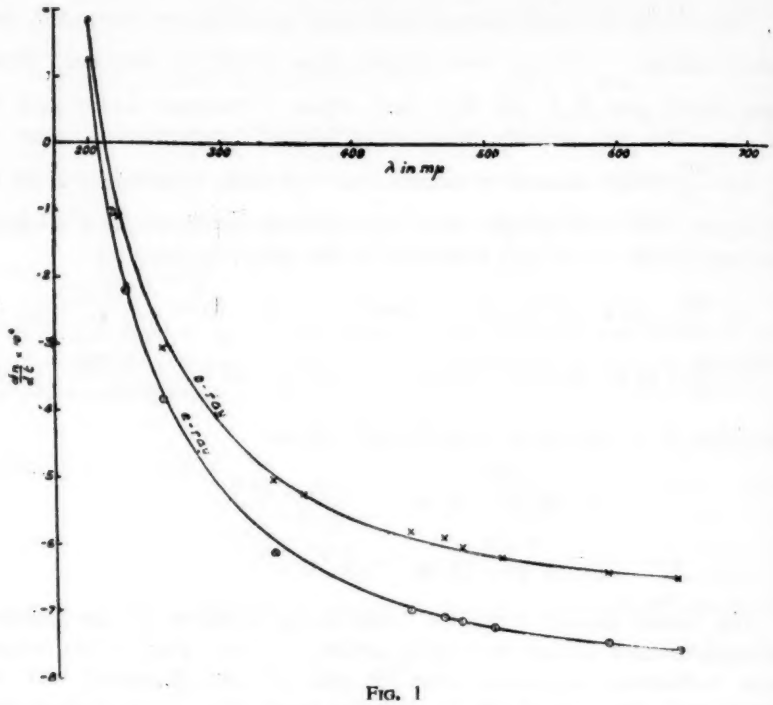

FIG. 1

The temperature coefficients $\left(\frac{dn_\omega}{dt}\right)$ and $\left(\frac{dn_e}{dt}\right)$ themselves vary with the temperature and we shall seek now to explain the variations on the basis of this theory. From our formula

$$2n\frac{dn}{dt}+\gamma_t(n^2-a)=A_t+\frac{B\chi_t}{(\nu_0^2-\nu^2)^2}$$

we get

$$\chi_t=\frac{(\nu_0^2-\nu^2)^2}{B}\left[2n\frac{dn}{dt}+\gamma_t\left(n^2-a-\frac{A_t}{\gamma_t}\right)\right] \tag{11}$$

Since $A_t=\frac{da}{dt}$ and a is partly a constant and partly proportional to the density, we can write $\frac{A_t}{\gamma_t}$ constant and this constant can be determined, knowing A_t at any temperature. Hence, if $\left(\frac{dn}{dt}\right)$ is known for various temperatures, χ_t can be evaluated as a function of temperature. The best data on $\left(\frac{dn}{dt}\right)$ as a function of t are those of Reed (1898). His values for the

ordinary ray at 60° C., however, differ systematically from the values of Micheli, on which the present formulæ are based. There is, on the other hand, good agreement in the case of the extraordinary ray. Calculations have hence been confined to the extraordinary ray.

On substituting numerical values in (11), the following formulæ result:

$$\left.\begin{aligned} -\chi_t &= 2.0535\left(\frac{dn_\epsilon}{dt}\right)_{\lambda 4358} + 1\cdot2155\,\gamma_t \\ -\chi_t &= 2.1760\left(\frac{dn_\epsilon}{dt}\right)_{\lambda 5893} + 1\cdot2155\,\gamma_t \\ -\chi_t &= 2.2067\left(\frac{dn_\epsilon}{dt}\right)_{\lambda 6563} + 1\cdot2970\,\gamma_t \end{aligned}\right\} \qquad (12)$$

The values of χ_t calculated from these formulæ are given below:—

TABLE III

Temperature (degrees C.)	$\gamma_t \times 10^6$	$\frac{dn_\epsilon}{dt}\,10^6$ (Rcd)			$-\chi_t \times 10^5$		
		4358	5893	6563	4358	5893	6563
23·0	34·35	− 6·52	− 7·14	− 7·18	2·84	2·84	2·87
61·2	35·6	− 7·07	− 7·66	− 7·73	2·88	2·89	2·91
125·2	37·7	− 7·71	− 8·29	− 8·43	3·00	3·02	3·03
177·0	39·35	− 8·73	− 9·33	− 9·44	2·99	3·01	3·02
227·5	41·1	− 9·52	−10·12	−10·30	3·05	3·00	3·06
275	42·65	−11·06	−11·78	−11·91	2·91	2·90	2·90
328	44·7	−13·48	−14·19	−14·27	2·66	2·63	2·65
385	47·3	−17·53	−18·40	−18·57	2·15	2·05	2·03
435	49·95	−21·49	−22·53	−22·75	1·66	1·49	1·46

Several interesting features are observed about this table. In the first place, the values of χ_t calculated from various wavelengths for the same temperature agree very well, thus confirming the soundness of the theory. χ_t is constant till about 300° C., and the value of 3×10^{-5} is the same as that calculated from the work of Nedungadi (1940) on the temperature variation of the fundamental Raman frequency shift 465 cm.$^{-1}$ in quartz, over the same range of temperature. This again illustrates the correspondence between electronic and lattice vibrations noticed by Ramachandran for a number of other substances. After 300° C., however, the value of χ_t falls off, contrary to the behaviour of the Raman line.

I express here my thanks to Sir C. V. Raman for his guidance in this piece of work.

5. Summary

The temperature variation of the refractive indices of quartz has been quantitatively explained on the basis of a theory put forward by G. N. Ramachandran and all the features observed, *viz.*, the reversal in sign of the coefficients in the ultra-violet, the variation of the coefficients with temperature and the difference between the coefficients for the extraordinary and ordinary rays are satisfactorily accounted for. The rate of shift with temperature of the characteristic ultra-violet frequencies of quartz near λ 1127 has been calculated for various temperatures. At about 60° C. $d(\log \nu)/dt = -2{\cdot}92 \times 10^{-5}$ which agrees with Nedungadi's value of $-2{\cdot}87 \times 10^{-5}$ for $d(\log \nu)/dt$ of the fundamental Raman frequency 465 cm.$^{-1}$ in quartz at that temperature, and is of the same order as Ramachandran's value of $-2{\cdot}5 \times 10^{-5}$ for $d(\log \nu)/dt$ of the ultra-violet absorption frequency at λ 1070 in vitreous silica.

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